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G. M. Shrum.

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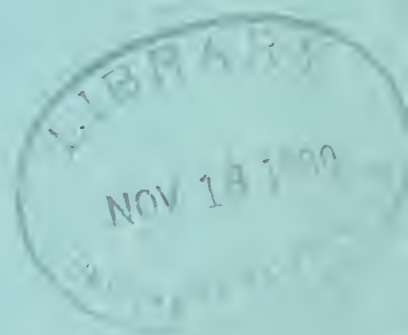
Studies in Spectroscopy  
and Low Temperatures.



Physics  
Optics  
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# Studies in Spectroscopy and Low Temperatures

BY  
G. M. SHRUM, M.A.



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*A thesis submitted in conformity with the requirements for the Degree of  
Doctor of Philosophy in the University of Toronto*





# *The Doublet Separation of the Balmer Lines.*

By G. M. SHRUM, M.A., University of Toronto.

(Communicated by Prof. J. C. McLennan, F.R.S. Received December 8, 1923.)

[PLATE 3.]

## *Introduction.*

According to the Bohr Theory the hydrogen atom consists of an electron in circular or elliptical motion about a positively charged nucleus. The steady states are defined by discrete values of the angular momentum and, in the case of elliptical motion, the eccentricities of the ellipses are limited to certain definite values. Sommerfeld, by an extension of Bohr's theory involving quantising both angular and radial momenta, has established the formula

$$\gamma = \frac{2\pi^2 m E^2 e^2}{h^3} \left[ \frac{1}{(T'_1 + T'_2)^2} - \frac{1}{(T_1 + T_2)^2} \right]$$

for the spectral series emitted by a system consisting of a nucleus with charge  $+E$  and an electron with charge  $-e$ . This is the familiar formula in which terms are included corresponding to elliptical as well as to circular motion for the revolving electron.

By the theory of relativity it can be shown that the mass of an electron in the elliptical orbit is not the same as its mass in the circular orbit, but that it depends on the velocity  $v$ , thus  $m = m_0 (\sqrt{1 - \beta^2})^{-\frac{1}{2}}$ , where  $\beta = \frac{v}{c}$  and  $m_0$  is the mass of the slow-moving electron. From a mathematical standpoint for a slow-moving electron we may consider the path as an ellipse with slowly moving perihelion. Applying this relativity correction, the above formula becomes

$$\gamma = NZ^2 \left[ \frac{1}{(T'_1 + T'_2)^2} + \frac{\alpha^2 Z^2}{(T'_1 + T'_2)^4} \left( \frac{1}{4} + \frac{T'_2}{T'_1} \right) + \dots \right. \\ \left. - \frac{1}{(T_1 + T_2)^2} - \frac{\alpha^2 Z^2}{(T_1 + T_2)^4} \left( \frac{1}{4} + \frac{T_2}{T_1} \right) - \dots \right]$$

where 
$$N = \frac{2\pi^2 m_0 e^4}{h^3}, \quad \alpha = \frac{2\pi e^2}{hc},$$

and  $Z = \text{Atomic Number.}$

For hydrogen we may put  $E = c$ . The Balmer series involves a two-quantum orbit for the final state, and thus if we put  $T'_1 + T'_2 = 2$  the formula becomes

$$\gamma = N' \left( \frac{1}{4} - \frac{1}{n^2} \right) + N_H \frac{\pi^2 e^4}{h^2 c^2} \left( \frac{T'_2}{4T'_1} - \frac{4T'_2}{T'_1 n^4} \right) + \dots$$

where 
$$N' = N_H \left[ 1 + \frac{\pi^2 e^4}{h^2 c^2} \left( 1 + \frac{1}{n^2} \right) + \dots \right].$$

Using this equation, Sommerfeld\* has shown that each member of the doublet  $H_\alpha$  should consist of a close triplet, each member of  $H_\beta$  of a close quartette, each member of  $H_\gamma$  of a close quintette, etc. He has also pointed out that for the two-quantum orbit, i.e.,  $T'_1 + T'_2 = 2$ , there are two possibilities, either  $T'_1 = 1$  and  $T'_2 = 1$ , or  $T'_1 = 2$  and  $T'_2 = 0$ . The value  $T'_1 = 0$  is barred, as it results in a linear motion through the nucleus. Thus the frequency for an electron falling into the circular orbit may be expressed as follows:—

$$\gamma = N' \left( \frac{1}{4} - \frac{1}{n^2} \right) - N_H \frac{\pi^2 e^4}{h^2 c^2} \cdot \frac{4T'_2}{n^4 T'_1} + \dots,$$

and for one falling into the elliptical orbit

$$\gamma = N' \left( \frac{1}{4} - \frac{1}{n^2} \right) - N_H \frac{\pi^2 e^4}{h^2 c^2} \left( \frac{4T'_2}{n^4 T'_1} - \frac{1}{4} \right) + \dots.$$

The frequency difference  $d\gamma$  of the doublets of the Balmer series is thus shown to be constant, and given by

$$d\gamma = \frac{1}{4} \frac{\pi^2 e^4}{h^2 c^2} N_H = 0.365 \text{ cm.}^{-1}.$$

It has been shown that in the case of  $H_\alpha$ ,  $H_\beta$  and  $H_\gamma$  the calculated distribution and intensities of the fine structural components are such that in actual determinations of the doublet separations, values somewhat less than  $0.365 \text{ cm.}^{-1}$  should be obtained. Thus in proceeding from  $H_\alpha$  to the higher members of the series, it would be expected, on the basis of the theory, to obtain for the doublet separation values slightly less for  $H_\alpha$ , but rapidly increasing to  $0.365 \text{ cm.}^{-1}$  for  $H_\delta$  and remaining constant for the higher members of the series.

Owing to the small mass of the hydrogen atom, a direct proof of Sommerfeld's theory by observation of the hydrogen lines is a somewhat difficult undertaking. As Foote and Mohler† have pointed out, the entire fine structure of the  $H_\alpha$

\* Sommerfeld, 'Atombau und Spektrallinien,' p. 344.

† Foote and Mohler, 'The Origin of Spectra,' p. 27.

line, as given by Sommerfeld, would cover a spectral range of only  $0.2 \text{ \AA.U.}$  The width of a spectral line, assuming it to be accounted for wholly by the Doppler-Fizeau effect, may be shown\* to be

$$\Delta = 0.86 \cdot 10^{-6} \lambda \sqrt{T/M}$$

where  $M$  is the molecular weight and  $T$  the absolute temperature of the radiating gas. Since  $M = 1$  for hydrogen, it is readily apparent that the Doppler effect will be quite pronounced and tend to mask any phenomena due to the fine structure. Even with the discharge tube immersed in liquid air, it can be shown that the theoretical width of each component of  $H_\alpha$  should be  $0.051 \text{ \AA.}$  Merton† has drawn attention to the effect of an electric field on the radiating particle, either imposed by the electrodes of the tube or the field due to the neighbouring atoms, as suggested by Stark.‡ Owing to these difficulties, the Sommerfeld theory has not as yet been confirmed by a direct observation of the fine structure of the hydrogen lines.

The helium atom, however, is four times as heavy as that of hydrogen, while the nuclear charge is double; so in consequence the separation of the doublets should be, according to the theory, 16 times as great. Paschen,§ by studying the spectrum of the ionised helium atom, found a good agreement between observation and theory. In applying these results to hydrogen he deduced that the separation for the hydrogen doublets should be given by  $d\gamma = 0.365 \pm 0.0045 \text{ cm.}^{-1}$ , exactly as Sommerfeld had predicted theoretically.

However, the main criticism of Sommerfeld's theory has not been that Paschen failed to find the lines exactly as predicted for the univalent helium atom, nor that all investigators have failed in their attempts to observe the fine structure of the hydrogen lines, but rather that there has been no agreement between the observed values of the doublet separation of the Balmer series and the constant value deduced theoretically by Sommerfeld. However, it should be noted here that the agreement among the observed values themselves is not better than the agreement between the observed and theoretical values.

\* Nagaoka, 'Proc. Math. Phys. Soc., Tokyo,' pp. 237-43 (1915); Lord Rayleigh, 'Phil. Mag.,' vol. 2, p. 274 (1915).

† Merton, 'Roy. Soc. Proc.,' A, vol. 92, p. 322 (1915).

‡ Stark, 'Elektrische Spektralanalyse Chemischer Atome' (1914).

§ Paschen, 'Ann. der Phys.,' vol. 1, p. 933 (1916).

Some of the experimental values are as follows :—

$H_{\alpha}$	$\Delta\lambda$ ( $\text{\AA}$ .U).	$\Delta\gamma$ (cm. <sup>-1</sup> ).
Michelson and Morley (1)	0.11	0.253
Fliert (2)	0.132	0.307
Michelson (3)	0.14	0.323
Houston (4)	0.065	0.153
Fabry and Buisson (5)	0.132	0.306
Messner (6)	0.124	0.288
Merton and Nicholson (7)	0.132	0.306
Merton (8)	0.145	0.34
McLennan and Lowe (9)	0.154	0.36
Gehrcke and Lau (10)	0.126	0.293
Geddes (11)	0.146	0.34
Oldenberg (12)	0.450	0.35

(1) Michelson and Morley, 'Phil. Mag.,' vol. 24, p. 46 (1887).

(2) Fliert, 'Wied. Ann. (N.P.),' vol. 43, p. 800 (1891).

(3) Michelson, 'Bur. Int. des Poids et Mesures,' vol. 11, p. 139 (1895).

(4) Houston, 'Phil. Mag.,' vol. 7, p. 456 (1904).

(5) Fabry and Buisson, 'C.R.,' vol. 154, p. 1501 (1912).

(7) Merton and Nicholson, 'Roy. Soc. Proc.,' A, vol. 93, p. 28 (1917).

(6) Messner, see Paschen, 'Ann der Phys.,' vol. 50, p. 933 (1916).

(8) Merton, 'Roy. Soc. Proc.,' A, vol. 97, p. 307 (1920).

(9) McLennan and Lowe, 'Roy. Soc. Proc.,' A, vol. 100.

(10) Gehrcke and Lau, 'Phys. Zeit.,' vol. 21, p. 634 (1920).

(11) Geddes, 'Roy. Soc. Proc.,' Edinburgh, vol. xliii, p. 37 (1922).

(12) Oldenberg, 'Ann. der Phys.,' vol. 67, p. 253 (1922).

$H_{\beta}$	$\Delta\lambda$ A.	$\Delta\gamma$ cm. <sup>-1</sup> .
Michelson	0.08	0.33
Merton and Nicholson	0.033	0.14
Merton	0.093	0.39
Gehrcke and Lau	0.0695	0.294
McLennan and Lowe	0.085	0.36
Geddes	0.078	0.33

$H_{\gamma}$	$\Delta\lambda$ A.	$\Delta\gamma$ cm. <sup>-1</sup> .
Gehrcke and Lau	0.058	0.31
McLennan and Lowe	0.062	0.33
Wood (*)	0.058	0.31

$H_{\epsilon}$	$\Delta\lambda$ A.	$\Delta\gamma$ cm. <sup>-1</sup> .
Gehrcke and Lau	0.043	0.26
McLennan and Lowe	0.049	0.29

\* Wood, 'Phil. Mag.,' p. 538, Sept., 1922.



On the whole, it will be seen that the values obtained are somewhat less than those demanded by the theory. In the case of some of the observations, the values indicate a steady decrease for the frequency differences as one passes to the higher members of the series. This would indicate that the Balmer series should be classified as a principal, rather than a subordinate, series.

This lack of agreement among the results of different observers has brought out much theoretical speculation, and many very refined experimental methods have been developed in the search for evidence that would lead to a confirmation or rejection of the Sommerfeld theory. Stark\* says that, according to the best experimental values both in hydrogen and helium, the Sommerfeld theory of the fine structure of the series lines will not satisfy the experimental results. He adds that, since the theory is based upon the Bohr quantum theory of the emission of spectral lines, together with an extension due to the special theory of relativity, and since the latter can be verified by many independent methods, therefore the former theory must be false.

It is evident that much of the variation in the results must be attributed to the difficulty in measuring the separation of the wide and more or less diffuse components of the doublets. Further, both Merton and Gehrcke and Lauf† have shown that it is possible to get various values for the separation depending upon the conditions under which the tube is excited. From this evidence it is not unreasonable to expect that the lines may be complex, consisting perhaps of three or more components, and quite in harmony with Sommerfeld's theoretical deductions.

The author, under very favourable conditions, has succeeded in photographing the doublet separations for the first five members of the Balmer series. In this work an arrangement was perfected whereby, when liquid air was used to reduce the Doppler effect, only light from the cooled section of the tube was allowed to fall upon the interference spectrograph. By this means very sharp photographs were obtained, and from these it was found possible to make a very precise determination of the doublet separation. It will suffice to state here that these results show that the doublet separation is not only constant but has a value almost in exact agreement with the theory of Sommerfeld.

\* Stark, 'Jahrbuch der Radioaktivität und Elektronik,' vol. 17 (1920).

† *Loc. cit.*

*Apparatus.*

The discharge tube (see Fig. 1) was made from clear fused quartz, and was somewhat similar to that used by Wood\* in photographing the higher members

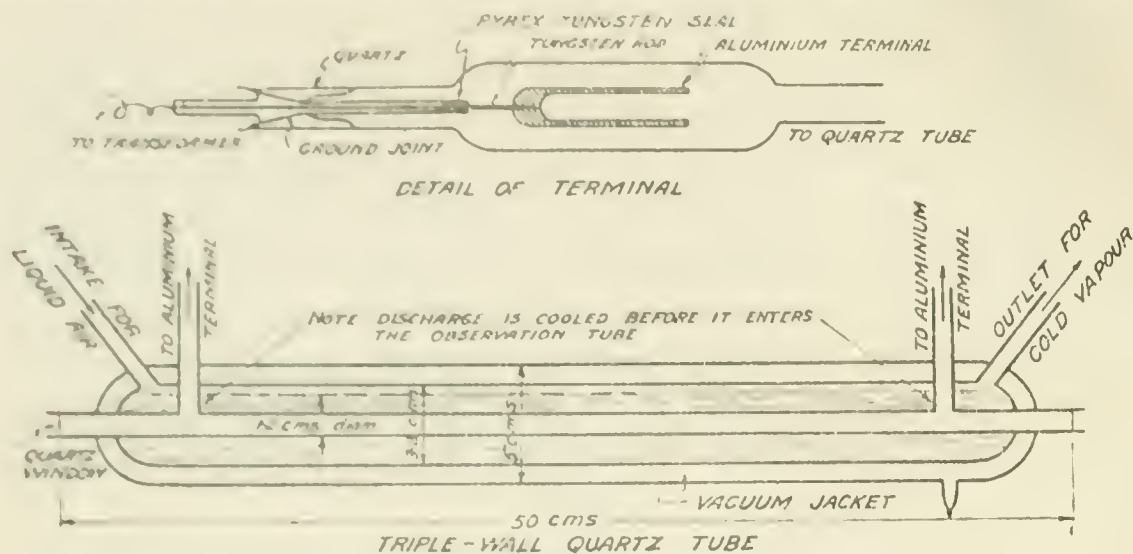


FIG. 1.

of the Balmer series. The central part of the tube consisted of a tube of quartz 1.2 cm. in diameter and 50 cm. long. A quartz window was sealed in either end of this tube, and two similar tubes bearing the electrodes were joined to it as shown in the diagram. The central tube was surrounded by two concentric quartz tubes, 3.8 cm. and 5 cm. in diameter. These were drawn down at the ends and sealed to the central tube. The closed space between these two tubes, when thoroughly exhausted and sealed, served to form a vacuum container suitable for liquid air or liquid hydrogen. It was found that when sound and durable seals had once been effected no difficulty was experienced from unequal contraction at the low temperatures. It is evident that the coefficient of expansion for quartz, although very small at ordinary temperatures, must fall off very rapidly for low temperatures. During the operation only the ends of the outer tube became coated with frost, and the extension provided for the windows insured that they remained clear at all times. This type of tube permitted a very economical use of the liquid air and liquid hydrogen, and thus it was possible to make comparatively extended observations at these low temperatures. The detailed drawing shows clearly the design of the electrodes and the method employed for sealing in the tungsten leads. The aluminium pieces were quite heavy, and were turned from a solid aluminium rod. This particular design prevented local heating effects in the

\* Wood, 'Roy. Soc. Proc.' A, vol. 97, p. 455 (1920).

surrounding quartz tube ; this was of particular importance when observations were made on the higher members of the series. In order to bring out these lines the tube was operated at very low pressures and high current values, and consequently the heating effect was considerable.

The hydrogen was introduced from a storage tank by means of a delicate micrometer valve, as shown in Fig. 2. It was carefully dried and purified by passing it over a number of tubes of cocoanut charcoal at liquid-air temperature.

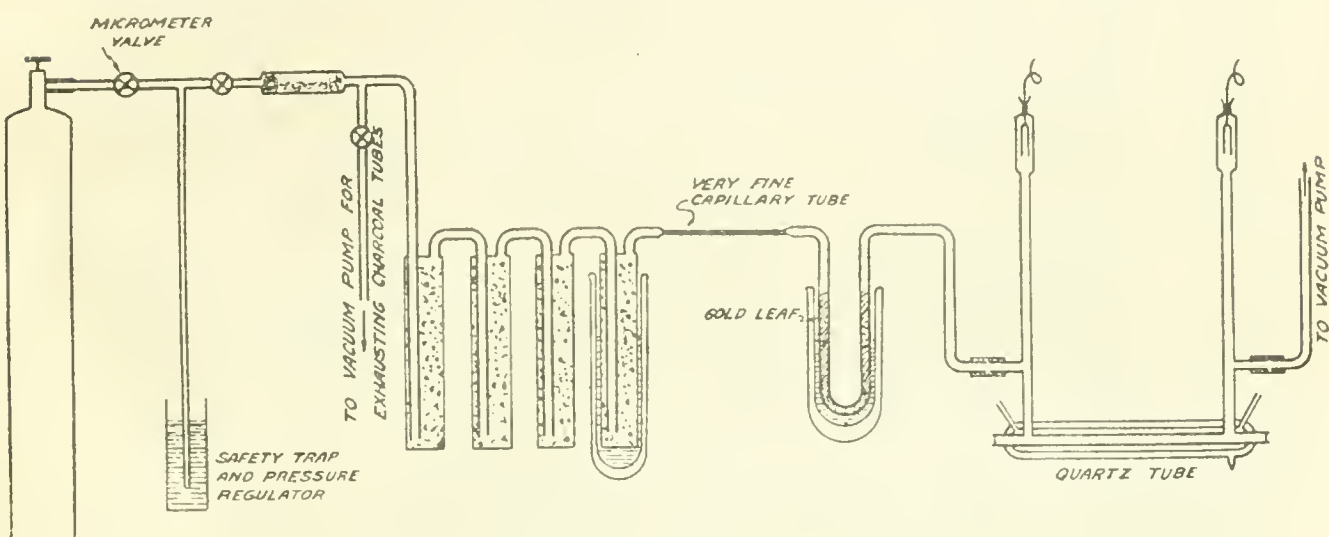


FIG. 2.

The discharge tube was protected from mercury vapour by means of two U-tubes filled with gold foil, and immersed in liquid air. These were placed in the gas cycle on either side of the tube. A Gaede rotary mercury pump was attached to the outlet of the discharge tube, as indicated in Fig. 2, and was kept continuously in operation whenever the tube was in use. Several methods of exciting the tube were tried, and the best results were obtained with a Wappler 100,000 volt X-ray transformer. The potential difference applied across the tube was varied by introducing resistance into the primary circuit. The transformer was operated on a 200-volt 25-cycle circuit, and the average current maintained in the primary was 20 to 30 ampères.

The tube was mounted so that the light from both ends could be examined simultaneously. During the operation of the tube a Hilger constant-deviation spectrograph was used to record, photographically, the purity of the gas and the relative intensities of the Balmer and secondary spectra. The light from the other end of the tube was examined by means of a Lummer plate, for which the optical data were the following : -



*Optical Data of Lummer Plate.*

## Refractive Indices.

	$\lambda(\text{\AA})$	$\mu$
$l = 13 \text{ cm.}$	6563.045	1.50746
$d = 0.148 \text{ cm.}$	5896.155 } 5890.186 }	1.50990,
$\frac{d\mu}{d\lambda} \text{ for } H_{\alpha} = -324 \text{ cm.}^{-1}.$	4861.49	1.51560
$H_{\beta} = 716 \text{ ..}$	4308.08	1.52025
$H_{\gamma} = 960 \text{ ..}$		
$H_{\delta} = 1150 \text{ ..}$		
$H_{\epsilon} = 1493 \text{ ..}$		
	The dispersion formula used	
$\Delta\lambda m \text{ for } H_{\alpha} = 0.4159 \text{ \AA.}$	$\mu 1.491324 + \frac{82.2922}{\lambda - 1463.17}$	
$H_{\beta} = 0.2224 \text{ ..}$		
$H_{\gamma} = 0.1755 \text{ ..}$	$\mu 1.494199 + \frac{69.3239}{\lambda - 2089.47}$	
$H_{\delta} = 0.1550 \text{ ..}$		
$H_{\epsilon} = 0.1518 \text{ ..}$		

The Lummer plate was mounted with its plane parallel faces vertical. The light used was that which issued axially from the central portion of the discharge tube. The mounting was arranged so that the position of the plate could be adjusted by means of graduated micrometer screws. By this arrangement a record of the various positions of the plate could be tabulated and a corresponding series of photographs taken.

*Qualitative Observations.*

At ordinary temperatures and with pure hydrogen it was found, as Wood\* has observed, that the transfer of energy from the secondary to the primary spectrum behaved very capriciously. Photographs showed that a great part of the energy of the discharge was represented as secondary spectrum. Observations in agreement with those of Merton and Wood were made, showing that the presence of water vapour was favourable to the production of the Balmer series with a corresponding decrease in intensity of the secondary spectrum.

It is now generally conceded that the Balmer series is produced by radiations from atomic hydrogen, while the secondary spectrum is due to the molecular formation. Wood has suggested that the potential applied to the tube is always

\* *Loc. cit.*



sufficient to dissociate the hydrogen, but that the walls of the tube and the electrodes act as a catalyser, and almost instantaneously change the atomic hydrogen back into molecular hydrogen.

The general theory is that water vapour acts as a poison to the catalytic action of the walls of the tube. However, at the temperatures for which water vapour could be used for the above purpose, the hydrogen doublets appeared so diffuse, owing to the Doppler effect, enhanced perhaps by the Stark effect, that no measurements on the separation were attempted. In order to reduce the Doppler effect, the central discharge tube was surrounded with liquid air. At this temperature, as Wood and Merton have also observed, nearly all the energy of the discharge comes out in the secondary spectrum. Only the  $H_\alpha$  and  $H_\beta$  lines appeared with sufficient intensity to be photographed as a Lummer plate pattern. The other lines of the series were lost in the practically continuous background due to the secondary spectrum.

The solution of the problem looked rather hopeless at the start, for it seemed that the devices used by Wood at ordinary temperatures, coupled with different methods of electrical excitation, variation of gas pressure, and many different methods of operation, would not transfer the maximum energy of the discharge into the Balmer series. The catalytic action of the walls of the tube seemed to be enhanced at the temperature of liquid air, and after many attempts to destroy it, the following method was adopted with considerable success:—

The central tube, after it had been thoroughly cleaned with hot chromic acid, and protected from mercury vapour as previously described, was cooled to  $-190^\circ\text{C}$ . by means of liquid air. Hydrogen containing a small percentage of air and at a pressure of about 5 mm. of mercury, was then passed through the tube. This impure gas was excited intermittently, by the discharge from the transformer, for a period varying from one to two hours. This insured that a very thin and even coating of water vapour was frozen on the inner walls of the tube. This layer of ice, together with the absorbed nitrogen, seemed to shield the atomic hydrogen from the catalytic action of the quartz walls. After this treatment, and while still at  $-190^\circ\text{C}$ ., the discharge tube and connecting apparatus were thoroughly exhausted, and pure hydrogen was introduced into the system. When the tube was subsequently excited, even with moderate currents, providing the temperature had been maintained at  $-190^\circ\text{C}$ . in the interval, the secondary spectrum appeared only near the electrodes and in the warmer sections of the discharge tube. When the light from the cooled section of the tube was examined through a direct-vision

pectrograph, the Balmer series appeared with great brilliancy against a practically black background. It required considerable practice in developing the technique of operating the tube before the secondary spectrum was so eliminated.

As is evident from Plate 3 the intensity of the secondary spectrum was not zero, but it was so small that no difficulty was experienced in isolating and photographing the Lummer plate patterns of the first five lines of the Balmer series. Spectra 2, 3, 4, 5, and 6 show the photographs of the Lummer plate patterns for the respective lines. The lines were comparatively sharp, and very little difficulty was experienced in measuring the doublet separations.

Many attempts were made to obtain the pattern for the sixth line of the series, but the results were always negative or doubtful, and no reliable measurements were obtained from them. It was comparatively easy to photograph  $H_\gamma$ , as it could be readily isolated by taking a series of photographs, starting with  $H_\alpha$ , which is in the visible region, and working towards the ultra-violet. A small camera requiring a short exposure was used to make a rough adjustment of the Lummer plate, and then with an exposure of from five to six hours with a larger camera, plates were obtained with sufficient density to give reliable measurements. The sixth line has only one-sixtieth of the intensity of the  $H_\gamma$  line, and as it lies relatively close to  $H_\gamma$  and has a much smaller intensity, it was not possible to obtain a sufficient density on the photographs of the Lummer plate pattern.

Attempts were made to get evidence of the fine structure of the lines, and with this end in view the tube was cooled with liquid hydrogen. At this temperature the energy again shifted to the secondary spectrum and the intensity of the Balmer lines decreased in proportion. Lummer plate photographs with the tube at this temperature were attempted, but they were not dense enough to be reproduced. The lines, however, were observed very closely, and as in all the previous cases, no evidence of any fine structure was noted. This seems to be in agreement with the work of Oldenberg.\* The satellites as observed by McLennan and Lowe and later by Geddes must therefore be attributable to the lines from the nitrogen or the secondary spectrum of hydrogen. These spectra were very intense in their photographs, as compared with the Balmer series, and it is possible that lines of an unknown origin may have appeared in the Lummer plate pattern of the Balmer lines.

\* Oldenberg, 'Ann. der Phys.,' vol. 67, p. 253 (1922).



6562.79

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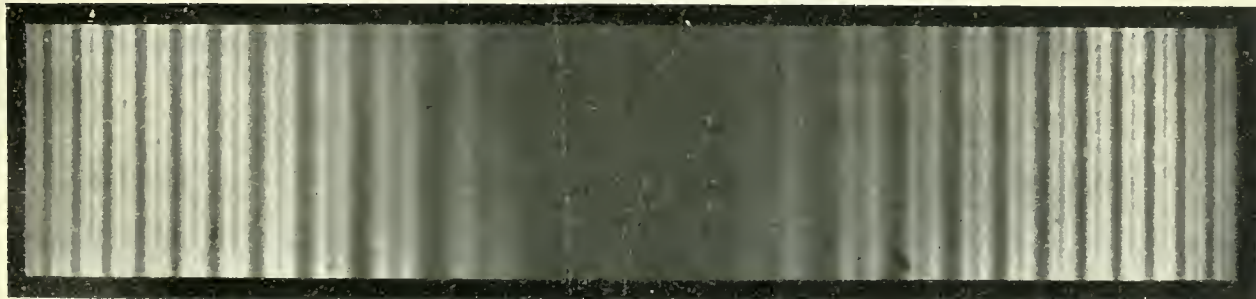
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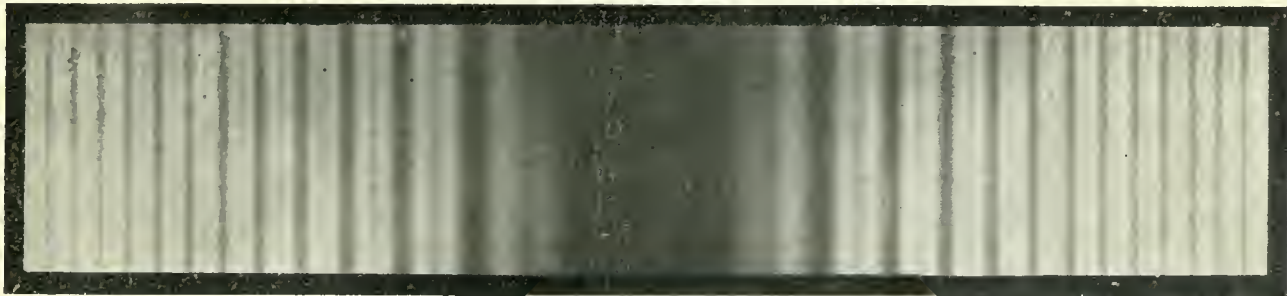
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$H_{\alpha}$        $\lambda = 6562.79 \text{ \AA.U.}$



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$H_{\beta}$        $\lambda = 4861.33 \text{ \AA.U.}$



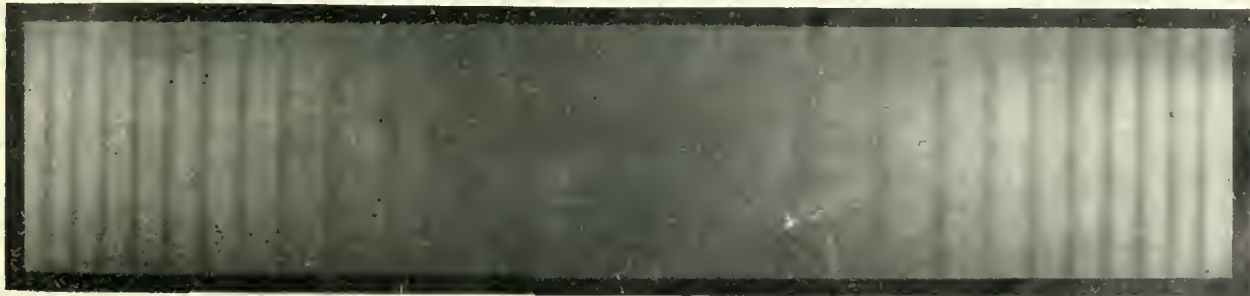
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$H_{\gamma}$        $\lambda = 4340.46 \text{ \AA.U.}$



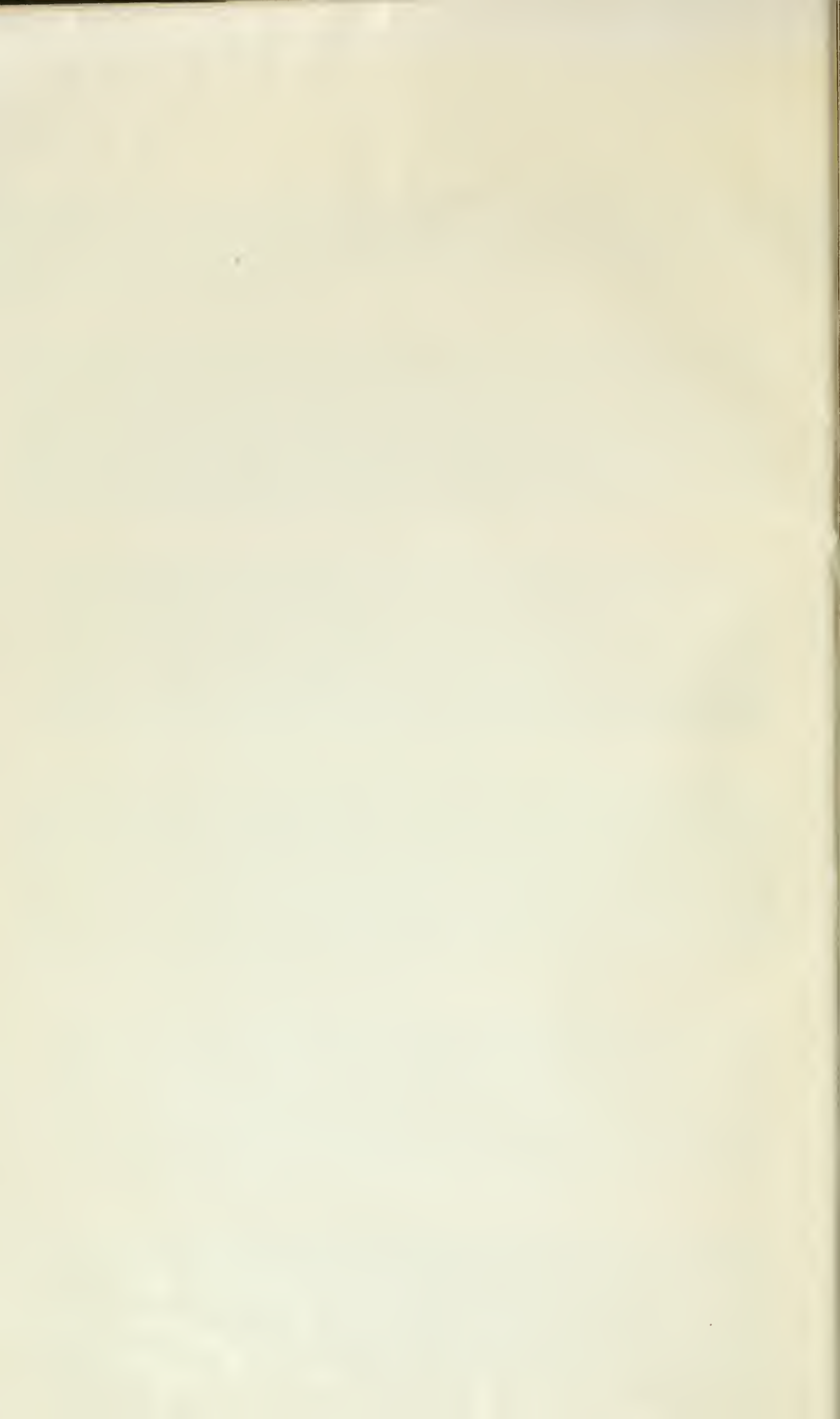
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$H_{\delta}$        $\lambda = 4101.73 \text{ \AA.U.}$



6

$H_{\epsilon}$        $\lambda = 3970.07 \text{ \AA.U.}$





*Quantitative Results.*

In measuring the plates a Toepler comparator was used. The measurements were made from the edges as well as the centre of the lines in the photographs, and the apparent optical centre was taken to correspond with the line of maximum density on the plate.

The readings from the various plates were taken as the average of three complete sets, each consisting of three settings on each line. It was found necessary to reduce the current considerably in order to get sharp doublets for the  $H_\alpha$  line, while the conditions for the other plates were always adjusted so as to give the maximum intensity for the line under examination.

The results of the measurements were as follows :—

<i>a</i> Line.	<i>b</i> Wave-length in Å.	<i>c</i> <i>d</i> Separation of the Components.		Probable Error.
		<i>d</i> λ.	<i>d</i> γ.	
H	6562·79	0·143 Å	0·33 cm. <sup>-1</sup>	±2·02
H	4861·33	0·085 „	0·36 „	±0·01
H	4340·46	0·070 „	0·37 „	±0·02
H	4101·73	0·061 „	0·36 „	±0·02
H	3970·07	0·055 „	0·35 „	±0·02

*Summary of Results.*

1. The doublet separations of the first five lines of the Balmer series have been determined and found to be almost in exact quantitative agreement with the theory of Sommerfeld.

2. A method has been described whereby the intensity of the Balmer lines relatively to the secondary spectrum may be increased many times, even when the discharge tube is at liquid-air temperatures.

3. No evidence of the fine structure was observed even under very favourable conditions.

4. The spectrum of pure hydrogen was studied when the discharge tube was at — 252° C. Evidence has been deduced to show that at this temperature the greater part of the gas is in the molecular condition.

*Conclusions.*

While it has been shown that a remarkable confirmation of Sommerfeld's theory has been obtained indirectly from Paschen's investigation of the structure of a number of wave-lengths in the spectrum of helium, and while it has been

shown that the L series of the Röntgen spectra of the elements consists of doublets with a constant separation between the components of approximately  $0.365 \text{ cm.}^{-1}$ , the present values for the doublet separations of the Balmer lines represent the first direct proof of the theory in so far as the atoms of hydrogen are concerned.

*Acknowledgments.*

The author wishes to thank all those who have so materially assisted in this work, and in particular Professor J. G. McLennan, who suggested the problem and placed at the author's disposal all the necessary equipment. Much credit is also due to Mr. Chappell, who so patiently and skilfully constructed the triple-wall quartz tube.

The author wishes also to acknowledge his indebtedness to the Honorary Advisory Council for Scientific and Industrial Research in Canada, who made this work possible by the award of a Fellowship.

*On the Liquefaction of Hydrogen and Helium*  
(II Communication)

By PROFESSOR J. C. McLENNAN, F.R.S., and G. M. SHRUM, M.A.  
University of Toronto

### I. *Introduction*

In a previous paper<sup>1</sup> by one of the authors, the details were given of an apparatus that had been designed and adapted in the Physical Laboratory of the University of Toronto for the liquefaction of hydrogen. This piece of apparatus proved to be quite satisfactory for preliminary work, but it has since been replaced by another of a somewhat modified design. The operation of a closed cycle for the liquefaction of hydrogen requires considerable experience and knowledge of technique, and in view of this it seemed advisable during the initial stages to construct the apparatus on a unit system. As the work progressed, however, and the preliminary plans made for the construction of a helium liquefier showed that possibly 30 to 40 litres of liquid hydrogen would be required at one time during the operation of the helium liquefaction cycle, the efficiency of the hydrogen liquefier became a matter of prime importance. It was therefore decided to modify the original apparatus and sacrifice simplicity of construction for efficiency in operation.

A second apparatus was consequently constructed. It has been thoroughly tested and has fulfilled all the exacting demands made upon it. A description of the apparatus and the method of operating it is given in Section IV.

The work on the design and construction of the equipment constituting the cycle for the purification and liquefaction of helium has also been completed, but an unfortunate delay in the delivery of suitable vacuum flasks makes it impossible at present to report a successful operation of this equipment. In Section VII there is given the details of the apparatus and the method we propose to follow in using it.

### II. *Compressors and Gasometers*

The hydrogen is compressed by means of a specially designed four-stage belt-driven compressor (see Fig. 1, also Plate I, 1) built by the Burckhardt Engineering Works of Basle, Switzerland. The cylinders are water-cooled, have a forced oil lubrication and are fitted

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<sup>1</sup>McLennan, Trans. Roy. Soc. of Canada, May, 1921.

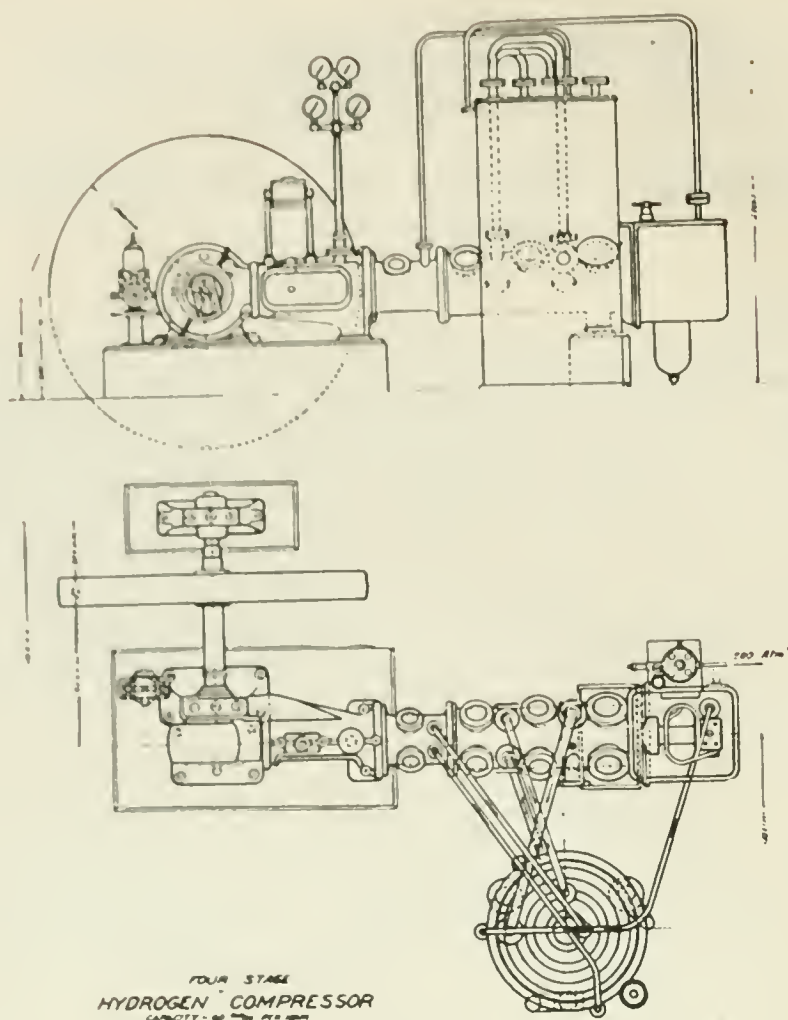
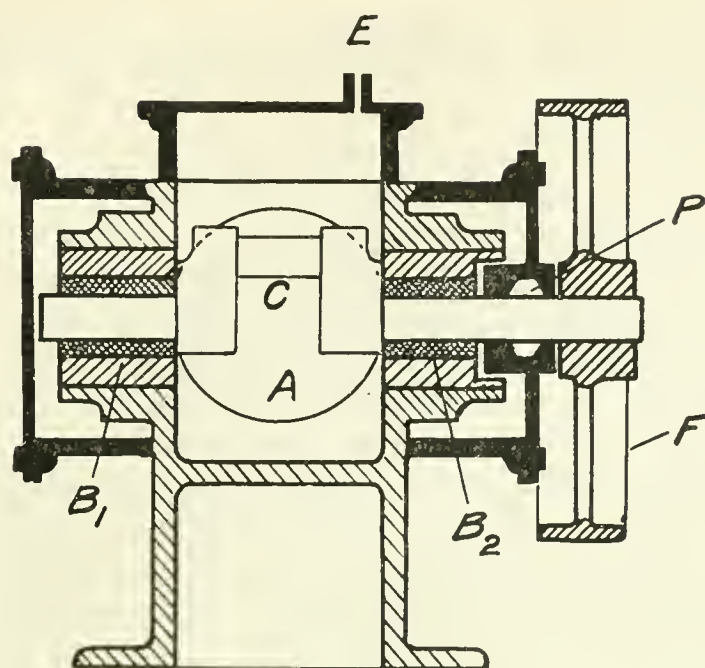


Fig. 1

with steel piston rings. The gas is cooled after each compression by means of a number of inter-coolers immersed in a tank of running water. The compressor is constructed so as to prevent any loss of gas, and with this end in view the piston rods are provided with special stuffing boxes in which the packing is sealed with oil holders. The space back of each piston, as well as the safety valves, are so arranged that they connect with the gasometer, and through the latter to the intake of the compressor. The compressor has a capacity of 60 cubic metre of free gas per hour, and requires a motor of 30 H.P. to operate it when delivering at 200 atmospheres pressure. Twenty litres of water per minute are disposed of by the inter-coolers.

We propose compressing the helium by means of a standard two stage Whitehead air compressor (Plate I, 2) that has been modified for use with rare gases (Plate I, 3). These modifications were made by completely enclosing the crank case with three castings electrically welded to the frame to which plates are bolted (Fig. 2). When the





*CROSS-SECTION SHOWING ADDITIONS  
TO WHITEHEAD COMPRESSOR*

Fig. 2

pump is in operation the crank case *A* is kept partially filled with oil so that as the crank revolves the bearings *B*<sub>1</sub> and *B*<sub>2</sub>, together with the stuffing box *P*, are well lubricated. The gas that leaks past the pistons of either the first or second stage is collected in this chamber, from which it is conducted through an oil-trap attached at *E*, to the low pressure intake.

The maximum capacity of this compressor is 600 cu. ft. of free gas per hour, but a simple and ready means of reducing this by any desired amount has been devised.

For the hydrogen cycle one gasometer of 60 cu. ft. capacity is installed, while for the helium cycle there are two with a capacity of 25 cu. ft. each. These gasometers are made from gauge No. 10 black iron, with welded seams, and an upper frame-work of channel iron. The gas-holders float on oil and are suspended by means of counter weights with roller-bearing pulleys. Since it is inadvisable to use any but a high grade oil the gasometers are arranged with an inner or third cylinder to reduce the amount of oil required. Glass check valves are arranged through which the oil of the gas-holder can be visibly drawn up and automatically checked. This latter arrangement eliminates the danger of crushing in the gas-holder or of pumping oil over into the piping system, should the pressure in the latter

become much less than atmospheric. The gasometers are joined to the piping system by means of wire-lined flexible gasoline hose.

### III. *The Hydrogen Cycle*

Plate 1 of the previous communication<sup>2</sup> plainly shewed the general arrangement of the hydrogen cycle. The installation represented in the above plate has undergone none but minor alterations, except for the gasometer that has been added to the low pressure system already described in Section II of this paper.

Ordinarily the gas is kept under pressure in steel cylinders tested to 200 atmospheres pressure. From the cylinders it is introduced by means of reducing valves into the gasometer from which it passes to the intake of the compressor. After compression the gas is passed through oil and water separators and then to the purifying or liquefying cycles, from whence it returns again at low pressure to the intake of the compressor. Extreme precautions are taken to prevent the escape or loss of gas in any manner. To this end all valves and unions are immersed wherever possible in heavy oil, that serves to indicate instantaneously a leak and prevents air from contaminating the system during the exhausting of the apparatus. By these means it is possible to run the cycle continuously without introducing more gas into the system than is required to replace that which is condensed as liquid. After each operation the gas is collected and compressed into the steel cylinders where it is safely stored until required.

### IV. *The Purification of the Hydrogen*

The commercial hydrogen that we are using may contain, we find, when manufactured electrolytically, as much as 1.5 per cent. oxygen and from 0.1 per cent. to 0.3 per cent. nitrogen. The presence of oxygen may be accounted for by the diffusion that takes place in the porous plates of the electrolytic cell, but the presence of nitrogen is due probably to contamination during the compression or storage.

In our operations the preliminary purification of the commercial hydrogen is effected by passing it through a high pressure bomb filled with palladiumized asbestos. This bomb is heated electrically to about 350°C. at which temperature the palladium acts as a strong catalyst, and the oxygen and the hydrogen combining to form water is later condensed in a trap or taken up by caustic potash. When the hydrogen at a pressure of 200 atmospheres is passed over this asbestos a number of times the content of oxygen in the hydrogen may be reduced to less than 0.1 per cent.

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<sup>2</sup>McLennan, Trans. Roy. Soc. of Canada, May, 1921.

Shakspear katharometers have been found to be almost indispensable for testing the hydrogen during the operation of the cycle, and while using them they are frequently calibrated and checked by means of hydrogen that has been chemically analysed, or tested by other physical means.

It is well known, however, that any trace of impurity in the hydrogen—other than helium—will be condensed and later solidified in the expansion coil of the hydrogen liquefier. Such condensation and solidification finally results in a complete stoppage of the expansion valve or of the tubes of the expansion coil. It is only possible, therefore, with other than absolutely pure hydrogen to make a limited amount of liquid hydrogen during each operation. In order to make 30 or 40 litres of liquid hydrogen without failure it is necessary to have available a large supply of extremely pure hydrogen. This is accomplished by an arrangement similar to that employed by Professor Kammerlingh Onnes in the Cryogenic Laboratory at Leiden.<sup>3</sup> It consists of an apparatus in which the gaseous impurities in impure hydrogen are condensed out by means of liquid hydrogen. Fig. 3 represents the apparatus schematically.

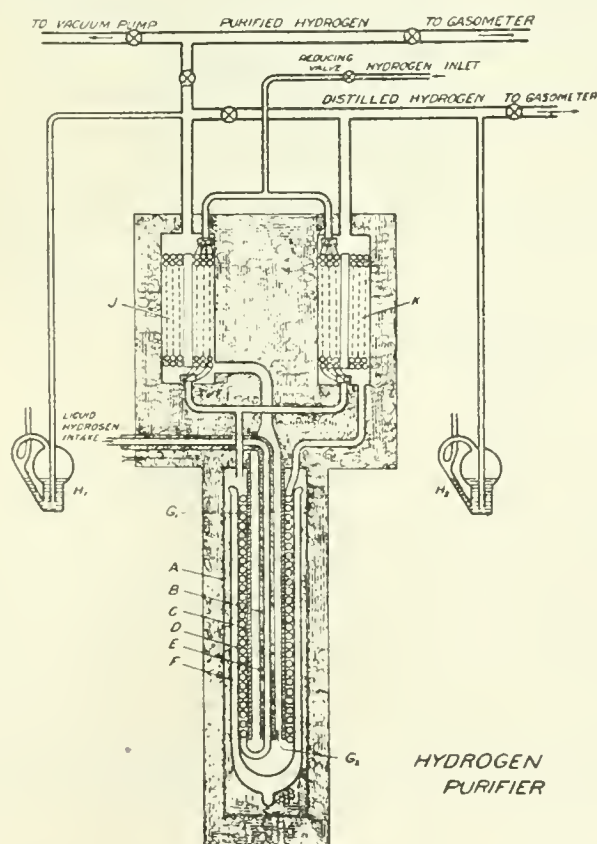


Fig. 3

<sup>3</sup>Kon. Akad. Weten, Amsterdam, 11, 1908-09.



Liquid hydrogen is siphoned into the apparatus through the insulated tube *E* to the lower end of the large spiral *D*. The hydrogen that is to be purified is controlled by a reducing valve, and enters the coils of the two exchangers *J* and *K* arranged in parallel. It then passes down over the outside of the spiral *D*. As the liquid hydrogen is continuously vapourized within this spiral the latter is kept at a very low temperature with the result that the gaseous impurities are condensed out upon the external surface.

The vapourized hydrogen rises in the spiral and passes out through the regenerator *K* to the gasometer. The purified hydrogen, upon reaching the bottom of the spiral, passes upward through a fibre tube and the regenerator *J* to the gasometer, from which it is compressed into cylinders.

A silvered vacuum flask *F* insulates the coil while a German silver cylinder *A* supports the flask and serves to keep the apparatus hermetically sealed. Thermocouples *G*<sub>1</sub> and *G*<sub>2</sub> serve to determine the rate of flow of the gas, since they indicate the temperature along the spiral. The arrangement of the connecting pipes is shown clearly in Fig. 3 in which *H*<sub>1</sub> and *H*<sub>2</sub> are mercury safety valves that protect the apparatus at all times. The purifier is entirely wrapped in wool and surrounded with a brass case as shown in Plate II, 1.

It is capable of purifying approximately 5 cubic metres per hour and requires in this time about 5 litres of liquid hydrogen. It is not suitable for work with hydrogen that has not undergone a preliminary purification, as during the operation all the impurity in the gas remains behind as solid, and is only removed at the close of the operation, when as the temperature rises the nitrogen or other impurities are drawn off by means of a vacuum pump.

#### V. *The Hydrogen Liquefier*

The liquefier is represented schematically by Fig. 4, while Plate II, 2 shows a photograph of the apparatus as it is installed in the Physical Laboratory at Toronto. It will be recognized that the principle of the construction is the same as that of the apparatus described in the first Communication from the Laboratory on this subject. The Joule-Thomson effect and Dewar's ingenious method of placing the regenerator coil in a vacuum flask are utilised. The regenerator coils are similar to those used in Hampson's apparatus for liquefying air. A number of features peculiar to the Leiden installation are also included.

Pure hydrogen is compressed to 200 atmospheres and cooled to  $-205^{\circ}\text{C}$ . by means of liquid air boiling under reduced pressure.



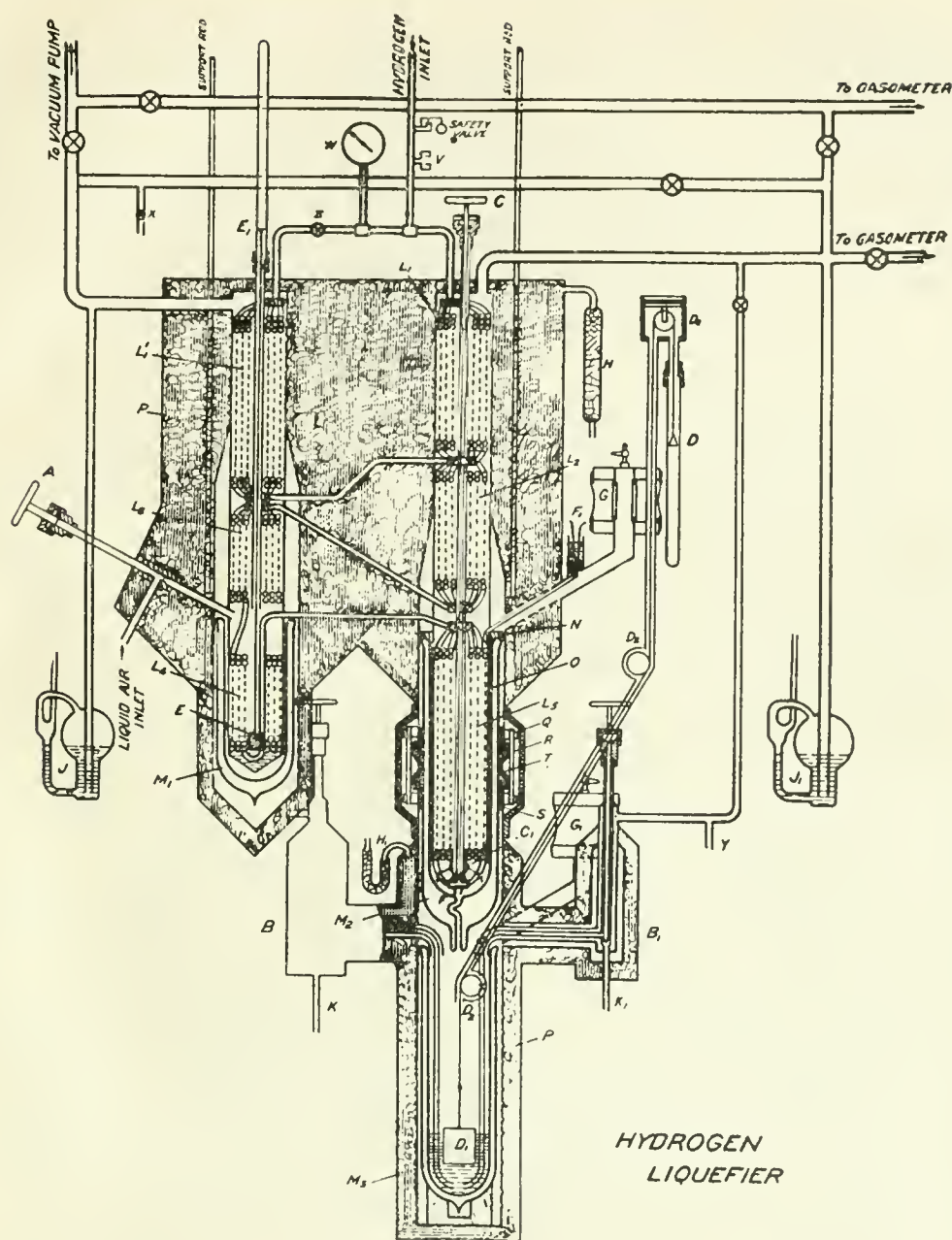


Fig. 4

The gas is then expanded from a nozzle and as a result of the regenerative cooling the temperature falls below the boiling point and liquid hydrogen is separated out.

The compressed hydrogen passess successively through the coils  $L_1$ ,  $L_1'$ ,  $L_2$ ,  $L_3$ ,  $L_4$ , and  $L_5$ , Fig. 4.  $L_1$  and  $L_1'$  are arranged in parallel and the valve  $Z$  serves to regulate the proportion of gas going through each of them. This insures the proper interchange of heat between the oncoming compressed gas and the out going low pressure vapours.

The coils  $L_1$ ,  $L_2$  and  $L_5$  are cooled by gaseous hydrogen returning to the gasometer from the expansion cock  $C_1$ .  $L_1'$  and  $L_3$  are cooled

by evaporated air being drawn off by the vacuum pump, and  $L_4$  is partially immersed in a bath of liquid air contained in the flask  $M$ . The valve  $A$  serves to admit more liquid air from the reserve flasks whenever the indicator  $E_1$  of the cork float  $E$  shows that it is required. The expansion or chief regenerator coil is well wrapped in flannel and still further protected by the double walled silvered vacuum flask  $M_2$ . The liquid, as it is formed, passes through the opening in the bottom of the flask  $M_2$  and is collected in the silvered flask  $M_3$ . The float indicator  $D, D_1, D_2$  serves to show the level of the liquid in this collecting flask. The weight  $D$  is connected with the thin German silver float  $D_1$  by means of a silk thread running over three pulleys  $D_2$  each with jewel mountings. Two valves,  $B$  and  $B_1$ , are used for drawing off the liquid. These valves are so arranged that they may be pre-cooled by the cold gaseous hydrogen that may be returned to the gasometer. The stuffing boxes and screw thread for the valves  $B, B_1, C$  and  $A$  are so arranged that they are not exposed to cooling and thus the danger of freezing is eliminated.

The insulation of the apparatus has been carefully studied. Vacuum flasks are used where possible and wherever parts are cooled below the temperature of liquid air, they are surrounded by an atmosphere of hydrogen or by a partial vacuum, in order to avoid unnecessary condensation. The regenerator coils are wrapped in flannel and fit snugly in German silver containers so as to insure a proper exchange of heat between the incoming and outgoing gases. All parts as far as possible are constructed of German silver, because of its low coefficient of thermal conductivity. The entire apparatus is packed in natural wool and enclosed in a thin brass case that is sealed except for the drying tubes  $H$  and  $H_1$ . These tubes serve to prevent water vapour from condensing and collecting inside. Fig. 4 shows plainly the arrangement for supporting the apparatus, together with the scheme of the pipe connections. Mercury traps  $J$  and  $J_1$  serve to protect the apparatus at all times from any excess of pressure, while rubber safety valves  $G$  and  $G_1$  serve to accommodate any sudden or violent increase in pressure.

When it is required to operate the cycle the complete system of piping, etc., is thoroughly exhausted. It is then filled with hydrogen and again exhausted, the operation being repeated until the hydrogen in the system is absolutely pure. The refrigerator surrounding the coil  $L_4$  is then filled with liquid air and the pre-cooling is effected by allowing the hydrogen to stream through at low pressure for some time. When the thermocouples indicate that the temperature of the hydrogen at the expansion valve is  $-205^{\circ}\text{C}.$ , the valve is gradually

closed until the pressure reaches 200 atmospheres. Some of the cold hydrogen is used to pre-cool the valves  $B$  and  $B_1$  and various other parts of the apparatus. As liquid is drawn off it is necessary to introduce fresh hydrogen into the gasometer. The liquefier will deliver 10 to 15 litres of liquid hydrogen per hour. The pre-cooling of the coils requires about 10 litres of liquid air per hour. Thus a very moderate supply of liquid air is quite sufficient for the production of a large quantity of liquid hydrogen.

#### VI. *The Helium and its Purification*

The helium was obtained by Professor McLennan from the natural gas of the Bow Island district, near Calgary, Alberta, in the year 1919-20, and has been kept since then safely stored in steel cylinders at about 150 atmospheres pressure. An analysis by means of absorption with cocoanut charcoal showed that it was about 90 per cent. pure. The impurity consisted chiefly of nitrogen with a varying percentage of methane. A Shakspear katharometer, such as is ordinarily used for hydrogen has been properly calibrated and is mounted for testing the purity of the gas during the operation of the cycle.

It is proposed to eliminate a large percentage of the impurity in the helium by means of the condensation produced as it is cooled by liquid air boiling under reduced pressure. In this manner, when the pressure of the helium is 150 atmospheres, the percentage of nitrogen may be reduced to less than 0.5 per cent. The remainder of the impurity other than hydrogen it is proposed to absorb by means of cocoanut charcoal at the temperature of liquid air. Traces of hydrogen are removed by absorption with  $\text{Cu O}$ , or burning with oxygen in the presence of palladiumized asbestos.

Fig. 5 shows the apparatus diagrammatically while Plate II, 3 is a photograph of the actual installation. The impure gas enters the outer tube of a spiral generator of the Linde type and passes thence through a spiral coil immersed in liquid air boiling at a pressure of 5 cms. of mercury. Any impurity that is condensed collects in the trap  $T$  while the purified gas passes through the central tube of the spiral regenerator to the valve  $V_1$ . The impurity from the trap is drawn off and collected through the micrometer valve  $V_3$ . An analysis of the gas that is collected serves to determine the quantity that should be drawn off. The level of the liquid air is shown by the indicator  $B$  of the cork float  $B_1$ . The valve  $M$  controls the supply of liquid air that is drawn over into the apparatus from the store bottles. Insulation for the apparatus is provided by a silvered vacuum flask  $F$



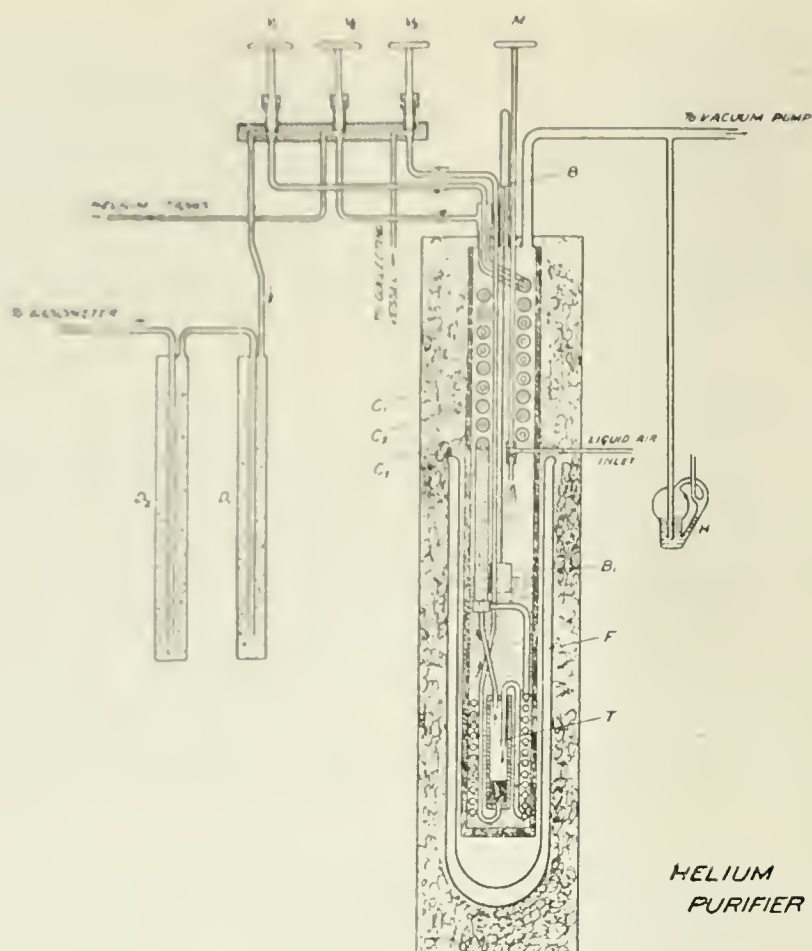


Fig 5

and a swathing of natural wool. After being partially purified in the manner indicated the gas is passed through the reducing valve  $V_1$ , and at low pressure through six cocoanut charcoal tubes,  $D_1$ ,  $D_2$ , etc. From these it is collected in the gasometer and finally compressed into tanks, to be introduced later into the liquefying system. In the construction of the apparatus care was taken to reduce its size to a minimum, so that the consumption of liquid air would not be very great, even although the alternate heating and cooling of the charcoal tubes necessitated our making the process of purification a discontinuous one.

#### VII. *The Helium Liquefier*

As the design of the hydrogen liquefier proved to be a highly efficient one it was deemed advisable to construct the helium liquefier on the same general principles, but on a considerably reduced scale. It will be recalled that in the operation of a helium liquefier, liquid hydrogen must be employed to cool the helium below the temperature at which the Joule-Thomson effect changes sign. When the gas is

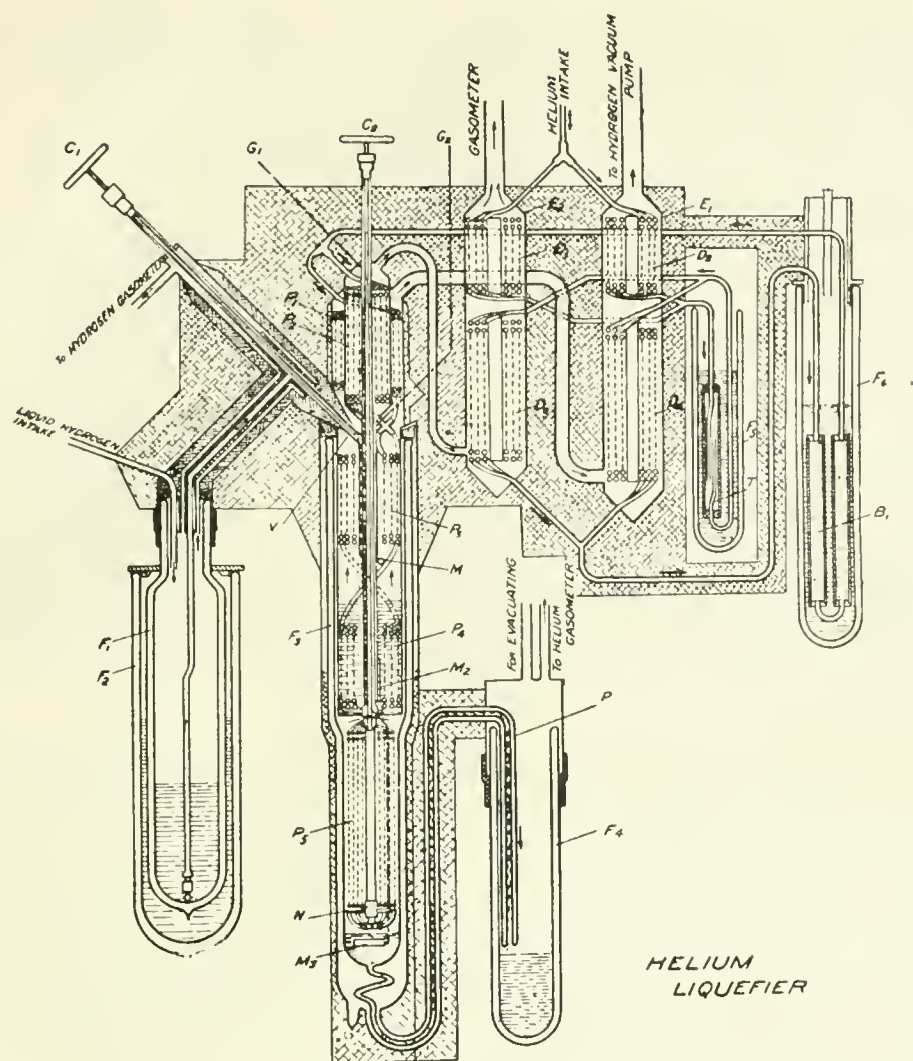


Fig. 6

reduced to this temperature it must then be expanded from a nozzle with the application of the principle of regenerative cooling. In the design of our helium liquefier provision was made for these features. The arrangement of parts is shown in Fig. 6.

The gas enters at the intake indicated in the figure. It passes successively through the coils  $D_1$ ,  $D_2$  and  $D_3$ ,  $D_4$  arranged in parallel. It then enters  $P_1$  and  $P_2$  also in parallel and afterwards passes successively through  $P_3$ ,  $P_4$ ,  $P_5$ .  $D_2$ ,  $D_4$ ,  $P_1$  and  $P_3$  are to be cooled by the vapourized hydrogen that is drawn off by the hydrogen vacuum pump.  $D_1$ ,  $D_3$ ,  $P_2$  and  $P_5$  serve as exchangers for the expanded helium. The coil  $D_4$  is to be partially immersed in liquid hydrogen boiling at a pressure of 5 cms. of mercury. The trap  $T$  is to be kept immersed in liquid air in order that the last traces of oil or water vapour coming from the pump may be condensed out.  $B_1$  and  $B_2$  are bombs to be filled with charcoal and kept at the temperature of liquid air so that

any gaseous contamination introduced into the helium in the working of the cycle may be removed. Provision is being made for indicating the level of the liquid hydrogen in the refrigerator by means of two constant volume helium thermometers with bulbs  $M$  and  $M_2$ . These bulbs are made of German silver and are to be connected to glass manometers by means of steel capillary tubing. The valve  $V$ , with its spindle  $C_1$  both pre-cooled with gaseous hydrogen, will enable one to regulate the supply of liquid hydrogen. The flask  $E$  that is to be used for storing a reserve supply of liquid hydrogen is not to be silvered and is to be kept immersed in a flask  $F_2$  filled with liquid air. This latter flask is to be provided with two unsilvered observation strips on either side to enable one to see the level of the liquid hydrogen directly. Provision is also made in the design for siphoning liquid hydrogen from the store bottles into the reserve flask  $F_1$  and since the vapourized hydrogen will necessarily be almost absolutely pure, provision has been made in the apparatus for carefully collecting and storing it.

The helium, as it is condensed on liquefaction, will collect in the bottom of the silvered flask  $F_3$  that is to be made with a specially designed delivery tube  $P$ . This tube will be double walled and silvered in the same manner as an ordinary vacuum flask. In this way it will be possible to transfer the liquid helium to the flask  $F_4$  or to any other suitable apparatus in which it may be required. In the design of the apparatus every precaution has been taken to prevent loss of helium or its contamination with hydrogen.

#### 8. *Summary*

In the statement above there are set forth the underlying principles, the design and many details as well of the equipment that will soon be completely installed in the Physical Laboratory of the University of Toronto for the purpose of liquefying hydrogen and helium.

NOTE.—While presenting this paper I desire to take the opportunity of acknowledging my very great indebtedness to Professor Kammerlingh Onnes of the University of Leiden, Holland.

The hydrogen purifier and liquefier, as well as the helium liquefier, were designed in accordance with drawings furnished to me by him. I also had the benefit of his advice in working out the details of the hydrogen compressor.

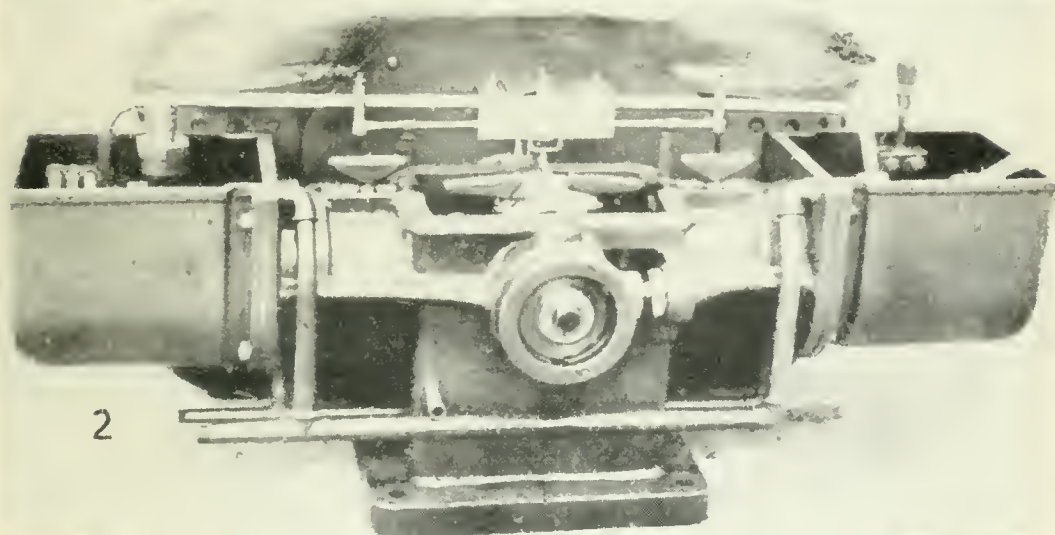
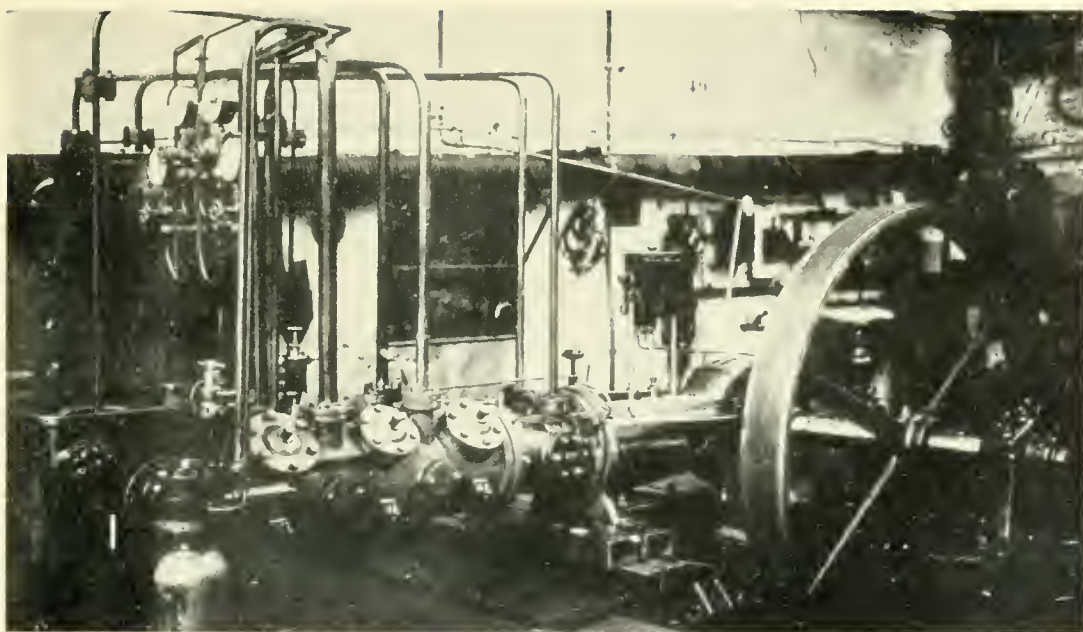


Through conversation and correspondence I gained much information from him that enabled me to expedite the construction and installation of our cryogenic equipment. To him I offer my sincere thanks.

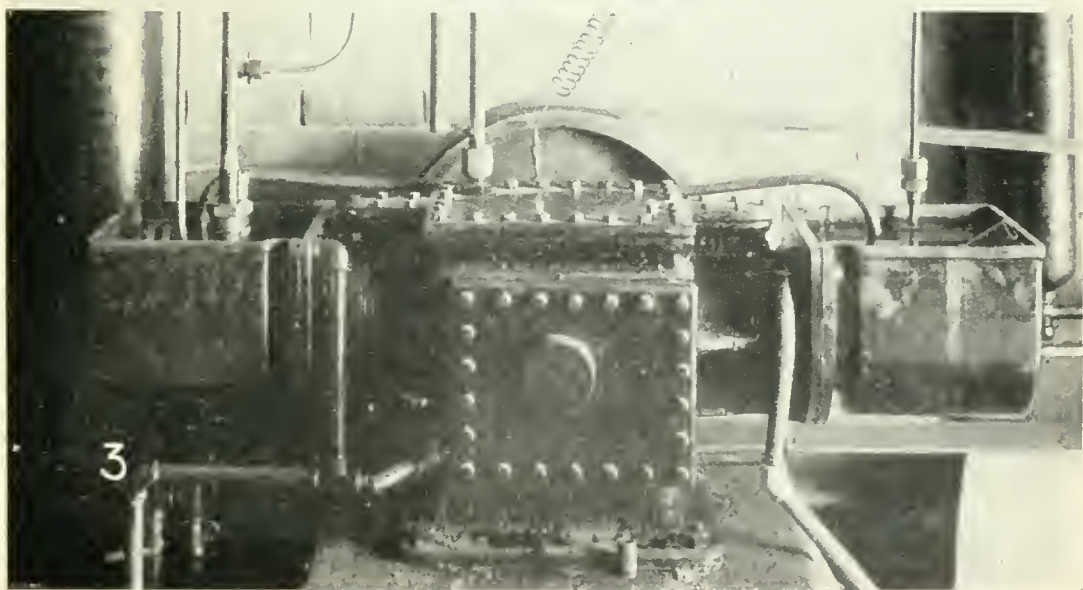
J. C. MCLENNAN.

Physical Laboratory,  
University of Toronto.  
June 15, 1922.





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PLATE I





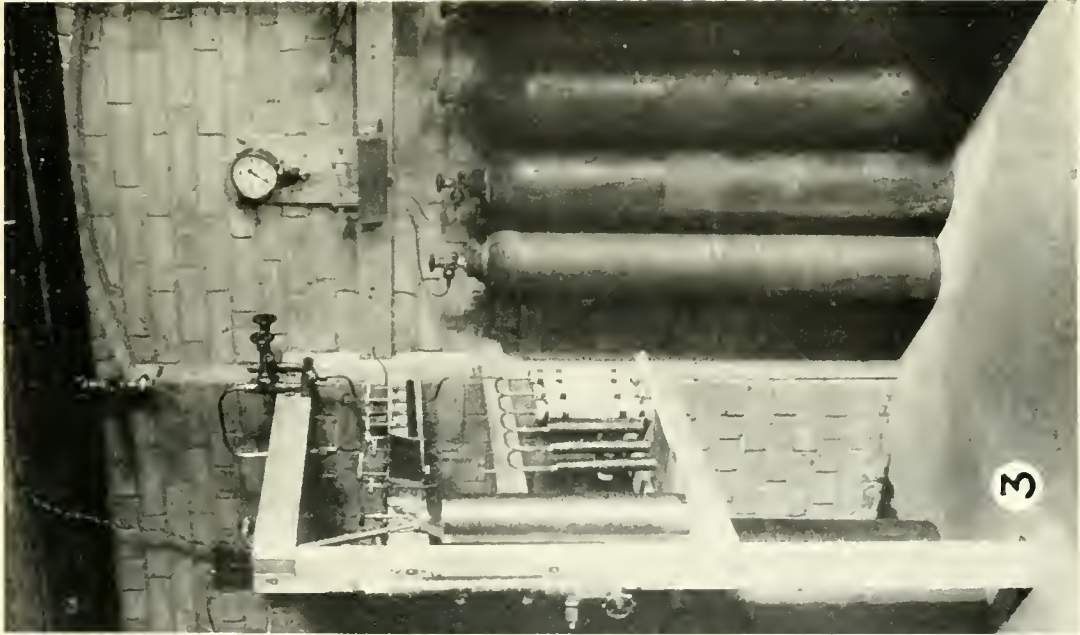
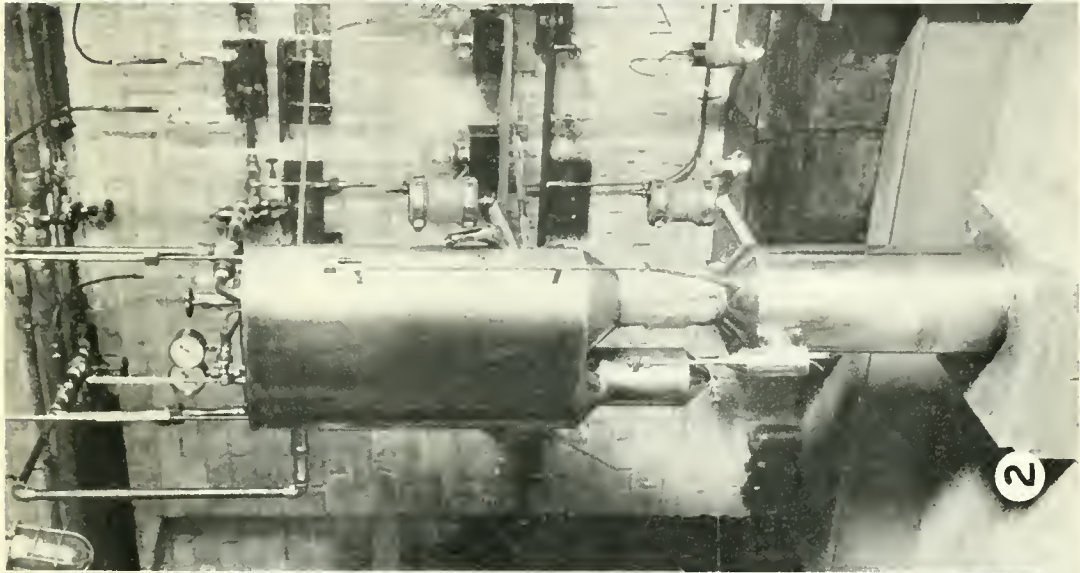
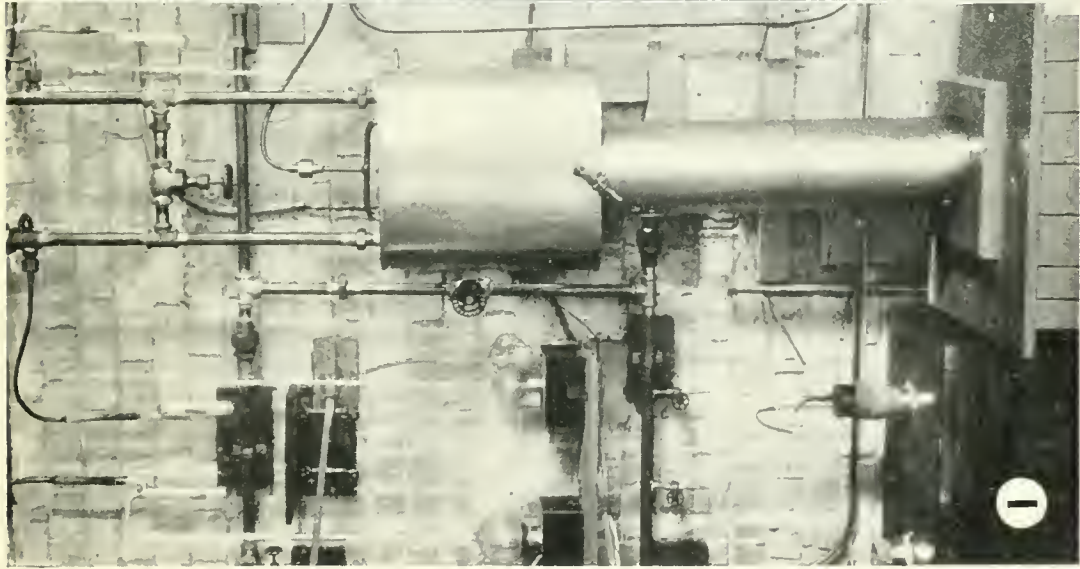
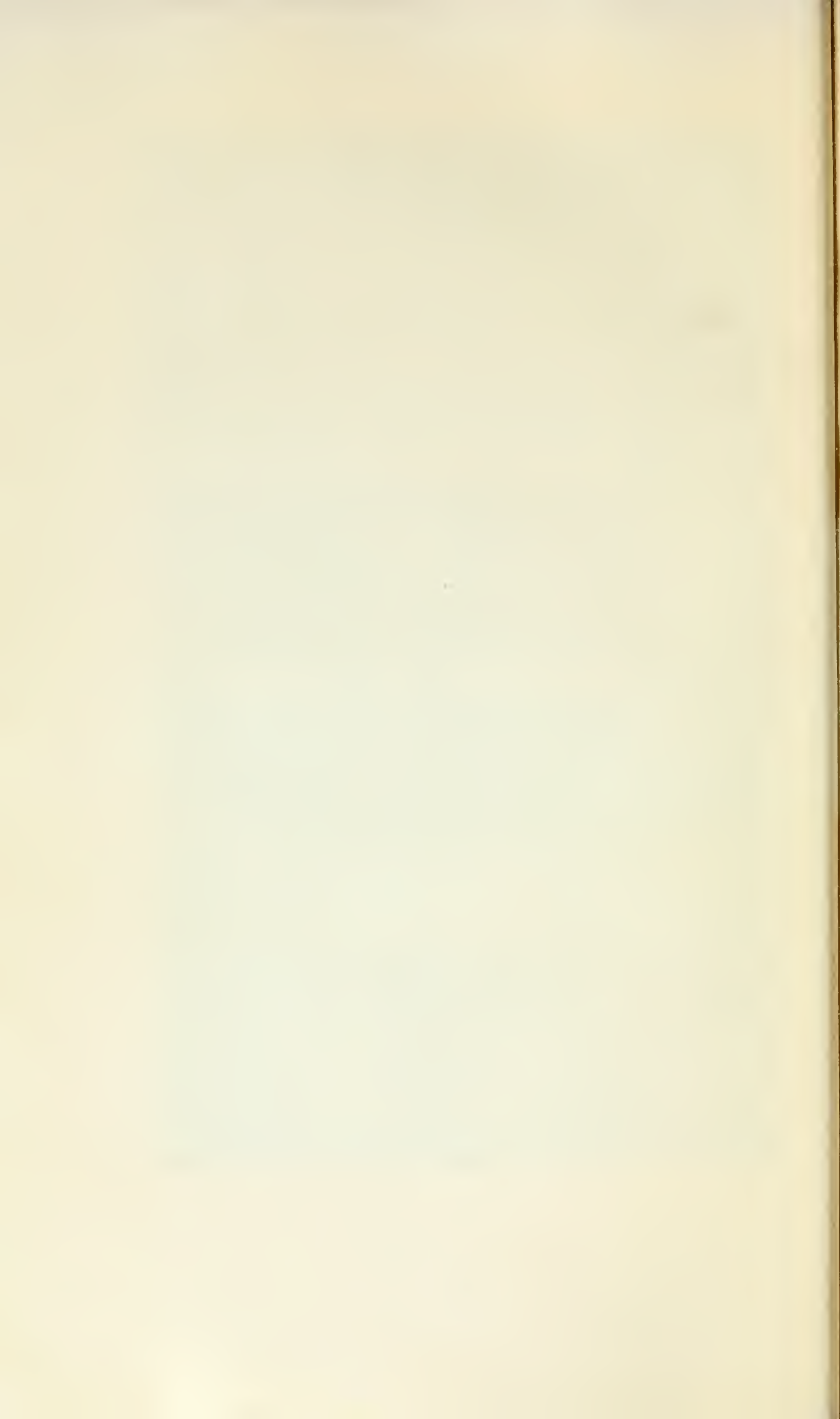


PLATE II





*On the Liquefaction of Hydrogen and Helium*  
(III Communication)

By PROFESSOR J. C. McLENNAN, F.R.S., and MR. G. M. SHRUM, M.A.,  
University of Toronto

*Introduction*

In two previous communications<sup>1</sup> detailed descriptions were given of the cryogenic equipment that had been designed, and installed in the Physical Laboratory of the University of Toronto. These communications described very fully the design and method of operation of the cycles for liquid air and liquid hydrogen.

I desire to state that Mr. G. M. Shrum was enabled to co-operate in this investigation through the award to him of a studentship kindly made by the Honorary Advisory Council for Scientific and Industrial Research of Canada. Also the expenses of a part of the investigation were covered by a grant made by the same Council, for which I am greatly obliged.

J. C. McLENNAN.

are very easily broken, sometimes accidentally and more often unavoidably; this is especially true of large cylindrical flasks. (2) They are limited to a small capacity, three litres being about the maximum. In order to overcome the excessive cost and inconvenience of breakages, and also to accommodate the large quantities of liquid air and hydrogen that are used in the laboratory, metal containers were introduced. These were purchased from well-established manufacturers, but proved to be very inefficient and consequently were not used extensively at first. Later, after it had become necessary to repair one that had been damaged, it was found that the efficiency, after being repaired, was some four times greater than that of any of those that had been purchased. Consequently all the containers were dismantled and reassembled. These then proved so efficient and

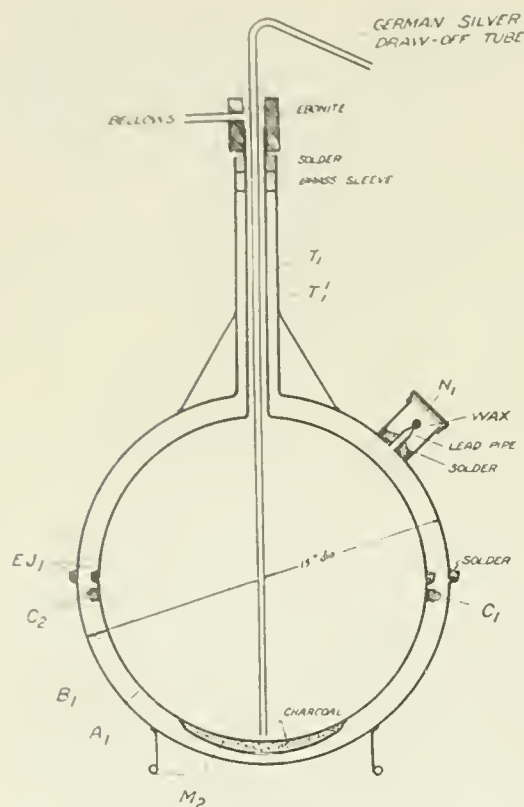
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<sup>1</sup>McLennan, Trans. Roy. Soc. of Canada, May, 1921.

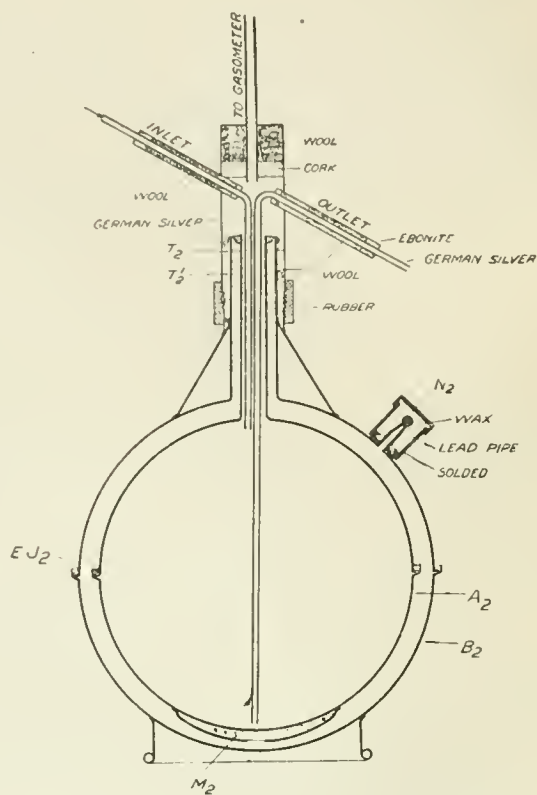
McLennan and Shrum, Trans. Roy. Soc. of Canada, June, 1922.

<sup>2</sup>January 10th and 24th, 1923.

satisfactory for storing liquid air, that they were tried with liquid hydrogen and after being slightly modified were found to be efficient containers of this liquid as well. Owing to their general usefulness wherever liquid air is to be used for research or laboratory purposes, some of the precautions that must be observed in the construction, assembling and subsequent exhaustion of them to insure a proper insulation, were deemed to be not without interest and are given below.



METAL CONTAINER  
FOR LIQUID AIR.  
FIG. 1



METAL CONTAINER  
FOR LIQUID HYDROGEN  
FIG. 2

Fig. 1 represents the flask for liquid air, and Fig. 2 the flask as it was adapted for liquid hydrogen. A good flask must be mechanically sound, and this soundness will depend upon the quality of the material and the skill of the workmanship employed in assembling it. The successful insulation depends upon (a) a correct polish and the maintenance of such under working conditions, (b) correct preparation and disposition of the absorbent material in the inter-space, (c) proper vacuum between the spherical shells, *A* and *B*, Figs. 1 and 2.

The spherical shells were made from copper spinings and when finished the metal walls of a five gallon container were about 0.032 inches thick. As copper has a high coefficient of reflection for infra-red rays the use of this metal for the spherical portions of the flasks

insured the elimination of heat losses arising from radiation. Sound and durable joints were required, especially at the equatorial junctions (see E.J. 1 and 2, Figs. 1 and 2 for the details of these junctions). This particular type of junction provided a ring of solder that reinforced the sphere. In addition, it was also very simple to make or dismantle. Special attention was paid to the soldering. Thorough tinning was required, and a soldering bit was used to make the joints, as a blow-pipe is very apt to overheat and tarnish the polished surfaces. As a flux, it was found that resin was the most satisfactory.

Little buffers of felt  $C_1$ ,  $C_2$ , Fig. 1, were used in the liquid air flasks. These gave support to the inner sphere, and when liquid air was being transported, lessened the strain on the soldered junction at the top of the neck of the flask. Owing to the small density of liquid hydrogen these buffers were not used in the flasks for transporting or holding this liquid. The tubes  $T_1$ ,  $T_2$  and  $T_2'$ , Figs. 1 and 2, were made of German silver while  $T_1'$  was of copper. The outer surfaces of  $A_1$  and  $A_2$  and the inner walls of  $B_1$  and  $B_2$  were highly polished. The parts  $M_1$  and  $M_2$ , Figs. 1 and 2, were each filled with about 6 ozs. of cocoanut charcoal. Since the charcoal was in contact with the surface of the container for liquid, it soon became cooled when the flask was filled with liquid air or liquid hydrogen and so provided a means of improving the vacuum between the walls. A short time before assembling the flask, the surfaces were buffed and all traces of the polishing powder removed. The flask was then immediately assembled and preliminarily exhausted. Various tests were employed to detect any trace of leakage. If the flask was found to be sound it was connected with a condensation pump and exhausted for six hours. During the whole series of evacuations the container was supported in an inverted position, and steam was continuously passed into the inner flask in order to drive off gases and water vapour adhering to the inner walls. The tube connecting the condensation pump to the flask was provided with a trap that was kept immersed in liquid air. By this means the water vapour driven off was condensed and held. Without this device it was found exceedingly difficult to remove water vapour completely. The sealing off was effected by pressing the walls of the heavy lead tube,  $N_1$ ,  $N_2$ , together. They were then scraped very clean, the flux was applied, the tube was cut off and its end dipped in molten solder. A five gallon container that had been properly exhausted would not lose more than 3 lbs. of liquid air per day. It was a matter of very great importance to see that the whole series of operations, from the assembling to the sealing off after



evacuation was continuous. It was found to be particularly important to have no delay between (1) the final polishing of the reflecting surfaces, (2) assembling, (3) transference of charcoal, after its heat treatment, to the containing vessel, and (4) the preliminary evacuation.

The connections for drawing off liquids from the containers are shown clearly in the drawing.

The draw-off tube of the container for liquid air was made by bending a 3/8" thin wall German silver tube to the required shape. A rubber stopper served to make the junction between the tube and the ebonite screw cap for the container. The tube that connected to the bellows contained a small safety trap. This served to protect the container from any sudden increase in pressure. The arrangement for the hydrogen container was a combination attachment that served both for filling the container with liquid from the liquefier and drawing off again when required. This eliminated the possibility of air condensing into the liquid hydrogen while the connections were being made. The tubes that conveyed the liquid were so arranged that they were surrounded by an atmosphere of hydrogen. The tubes were made from 3/16" German silver tubing, with a wall .012" thick. The rubber sleeve served a dual purpose in that it effected an airtight junction for the working pressures and expanded to act as a safety valve for higher pressures.

*(b) Some Additional Features of the Hydrogen Cycle*

The hydrogen liquefier described in Communication No. II (Plate I "a" is a photograph taken in the laboratory) was found to operate most satisfactorily when used with extremely pure hydrogen. Experience in operating the cycle, has justified all the extreme precautions that were taken in the original design for insuring the purity of the hydrogen. It was found advantageous to add to the cycle as an auxiliary purifier a large tube filled with cocoanut charcoal. This tube was arranged so that it could be heated and exhausted independently of the regular cycle. After the liquefier and conduits were exhausted and filled with pure hydrogen, the gas was circulated by means of a side conduit through this charcoal tube immersed in liquid air until it was freed of the last traces of impurity, that remained in the compressor and conduits.

It was also found advantageous to change the high pressure gauge  $W$  (Fig. 3) so that it indicated the pressure at  $W_2$  instead of  $W_1$ . By this change, better control of the expansion valve was

obtained, and the possibility of a too sudden expansion at the nozzle with consequent breaking of the safety valves was avoided. The efficiency of the liquefier was improved by providing the expansion coil  $L_5$  with a close-fitting German silver envelope. This envelope when it was properly wrapped with flannel, permitted a better junction to be effected between the inner wall of the glass flask  $M_2$  and the coil, and consequently insured that more of the expanded gas passed over the closely wound tubes of the coil and thus better regeneration was obtained.

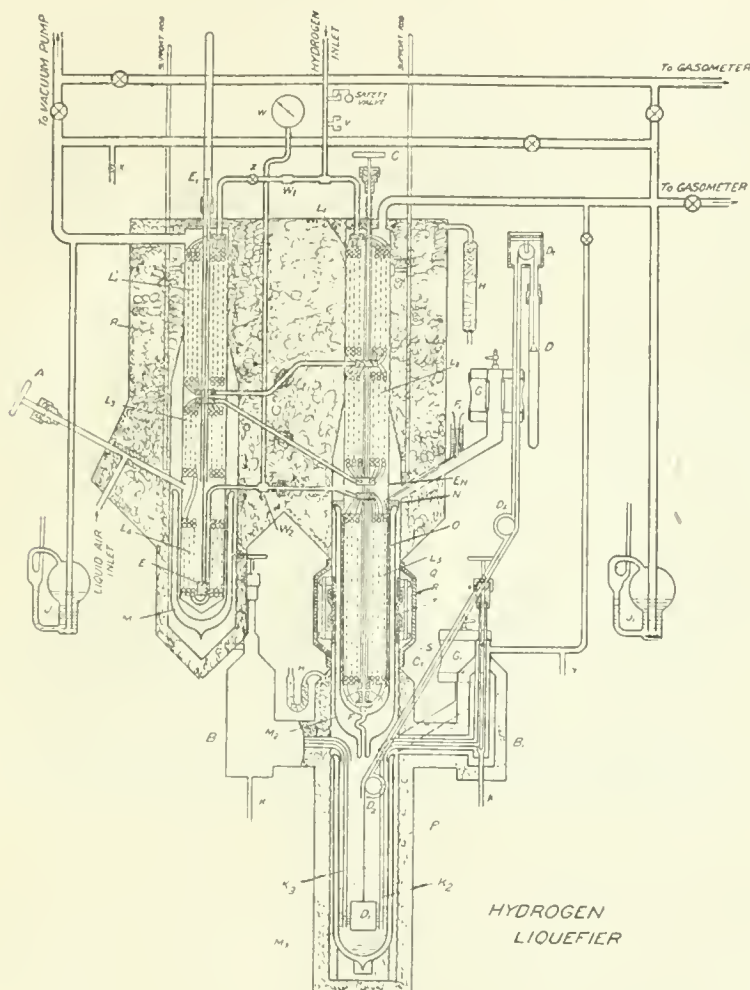


FIG. 3

It was found that at times a very slow accumulation of solid impurity in the flask  $M_3$  caused great inconvenience by blocking the draw-off valves  $B_1$  and  $B_2$ . This was overcome by shortening the tubes  $K_2$  and  $K_3$  so that they are about 2 cms. clear of the bottom of the flask  $M_3$ .

The hydrogen purifier shown in Fig. 3, Communication II, was found to be quite satisfactory as a purifier, and it had an additional

advantage in that it was very useful as a vaporizer, when it was required to evaporate and store small quantities of liquid hydrogen that were left over from experiments. It was found, however, that the commercial hydrogen that was used contained as an impurity at times, as much as 3% of air. This proved very troublesome, since after the hydrogen was passed over the palladiumised asbestos there was still a large percentage of nitrogen in it as an impurity. Absorption with cocoanut charcoal at liquid air temperatures proved to be the most economical method for freeing the hydrogen of this nitrogen, as a preliminary purification to the more refined method described in Communication II. The details of an installation for this purpose were very carefully worked out, and since the method proved so efficient and economical for the purification of large quantities of gas, a short description of the apparatus is included here. Proper insulation in conjunction with efficient heat exchangers served to keep the consumption of liquid air to a minimum. Good insulation was effected by (1) the compactness of the design, (2) the use of steel vacuum vessels, and (3) by a copious swathing of natural wool. The exchangers were of the proper dimensions so that when used in conjunction with the two delicate reducing valves,  $V_1$  and  $V_2$ , the outgoing gases were always at room temperature. The scheme of the apparatus is shown in Fig. 4. The hydrogen was taken from the high pressure cylinders through the two reducing valves  $V_1$  and  $V_2$  and then entered the coils of the two exchangers  $E_1$  and  $E_2$ . From the exchangers it passed through the two charcoal containers in series (as indicated by the arrow) and then to the exchanger  $E_2$ , where as it passed up, around the outside of the coils, to the gasometer it robbed the oncoming hydrogen of its heat energy. Liquid air was supplied to the two steel vacuum flasks  $F_1$  and  $F_2$  by means of the valves  $M_1$  and  $M_2$  as indicated in the figure. The charcoal containers were wrapped with asbestos cloth and were provided with permanent heating coils with leads at  $L_1$  and  $L_2$ . Cork floats  $B_1$  and  $B_2$  indicated the level of the liquid air in the containers, while the thermo-couples  $T_1$  and  $T_2$  indicated the temperature of the charcoal during the exhaustion. A katharometer placed at  $K$  was used to determine the purity of the outgoing hydrogen. The apparatus was found to operate very satisfactorily. From 100 to 300 cubic feet of hydrogen was purified before the charcoal required heating and re-exhausting. The complete cycle for purification was as follows: The commercial hydrogen was first passed over the heated palladiumised asbestos, and thus freed of its oxygen content. This eliminated any danger from explosions due to any accumulation of oxygen in the charcoal



or any other part of the equipment. The gas was then passed through the charcoal purifier described above and afterwards to the final purifier described in Communication No. II.

(c) *The Liquefaction of Helium*

(1) *Method.*—The Joule-Kelvin effect is the most important factor in the liquefaction of those gases whose critical temperatures lie very low. When expansion from a nozzle is utilized for the

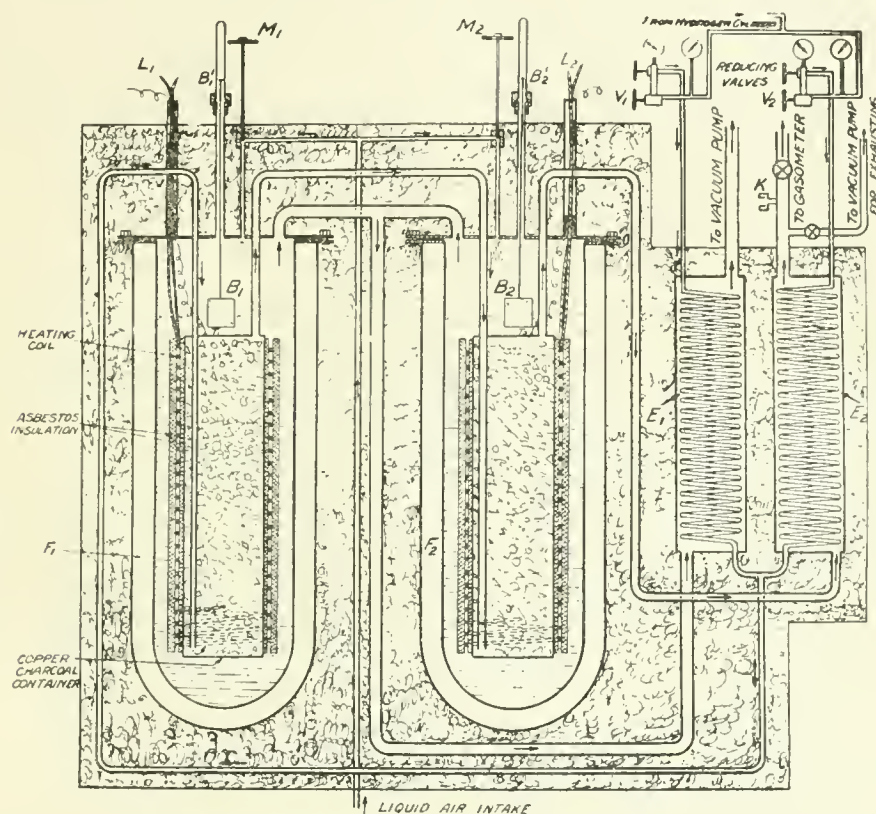


FIG. 4 CHARCOAL PURIFIER FOR HYDROGEN

liquefaction of a gas, the latter must first be cooled below the temperature at which the sign of the Joule-Kelvin effect is negative. Theoretically, when a gas is cooled below this temperature, called the inversion temperature, liquid may be obtained by an adiabatic expansion. Practically, however, it is found that if the gas is not cooled somewhat below this temperature, the Joule-Kelvin effect will not have a sufficient value for a statical liquefaction process to succeed.

The work of Kammerlingh Onnes<sup>1</sup> on the determination of the isotherms of helium at low temperatures, in conjunction with specific

<sup>1</sup>Kon. Akad. Amsterdam, 11, 1908-9.

heat determinations, has shown that the inversion point for helium lies between  $-252^{\circ}\text{C.}$  and  $-259^{\circ}\text{C.}$  and sufficiently above  $-259^{\circ}\text{C.}$  to insure sufficient cooling for a statical liquefaction process to succeed at  $-259^{\circ}\text{C.}$ , practically the lowest temperature that is possible with liquid hydrogen.

Knowing that the principle was correct and that the present hydrogen liquefier was a highly efficient one, it was decided to build the helium apparatus upon the same general principles, but on a considerably reduced scale. The expansion coil was reduced until its dimensions were only about  $1/3$  those of the ordinary Hampson coil. This reduction in the internal diameter of the tubes necessitated even more refined methods of purification than had been employed in the hydrogen cycle. In the design and construction every precaution was taken to provide adequate insulation. The exchangers and connecting tubes were wrapped with several layers of flannel and this in turn bound with rubber tape. The whole apparatus was packed in clean wool and surrounded by a polished brass case—as indicated in Fig. 6. Care was taken to ensure that all parts that became cooled below  $-185^{\circ}\text{C.}$  during the operation, did not come in contact with the air.

(2) *The Helium and its Purification.*—The Helium was obtained by Professor McLennan from the natural gas of the Bow Island district near Calgary, Alberta, in the year 1919-20, and had been kept since then safely stored in steel cylinders at about 150 atmospheres pressure. A preliminary analysis by means of absorption with cocoanut charcoal showed the gas to be from 90% to 95% Helium. The chief impurity was nitrogen with varying percentages of methane and other gases. Mr. R. J. Lang<sup>1</sup> carried out a series of very careful analyses of the gas for hydrogen and was unable to detect any hydrogen by means of chemical absorption methods or explosion with oxyhydrogen gas. His apparatus was so arranged as to detect .05% of hydrogen in previously prepared mixtures. He also calibrated 2 Shakespear katharometers<sup>2</sup> for use with helium, one for low purity gas and the other for high percentages of helium. These were calibrated by means of the density balance and explosion methods.

The preliminary purification of the Helium was effected by cooling it, at a pressure of 150 atmospheres, to  $-205^{\circ}\text{C.}$  by means of liquid air, boiling at reduced pressure. Under these conditions a large percentage of the impurity was condensed and drawn off. The

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<sup>1</sup>Lang, Trans. Roy. Soc. of Canada, 1923.

<sup>2</sup>Murray, Trans. Roy. Soc. of Canada, 1919.

remainder of the impurity, other than hydrogen, was then absorbed by cocoanut charcoal at the temperature of liquid air.

Fig. 5 represents schematically the cycle for the purification. The gas was led from the cylinders through the corresponding valves, these were immersed in water for the detection of leakage, and entered the outside tube of the Linde regenerator coil at *P*. As the gas was cooled to  $-205^{\circ}\text{C}$ . in the spiral coil *R* immersed in liquid air boiling under reduced pressure, a large percentage of the impurity was condensed in the trap *T* and drawn off by means of the micrometer valve *A*<sub>4</sub>. An analysis by the katharometer marked *L.P.* served to determine the quantity that should be drawn off. The helium was passed through the reducing valve *A* 1<sub>m</sub> to six charcoal tubes *C L P*,

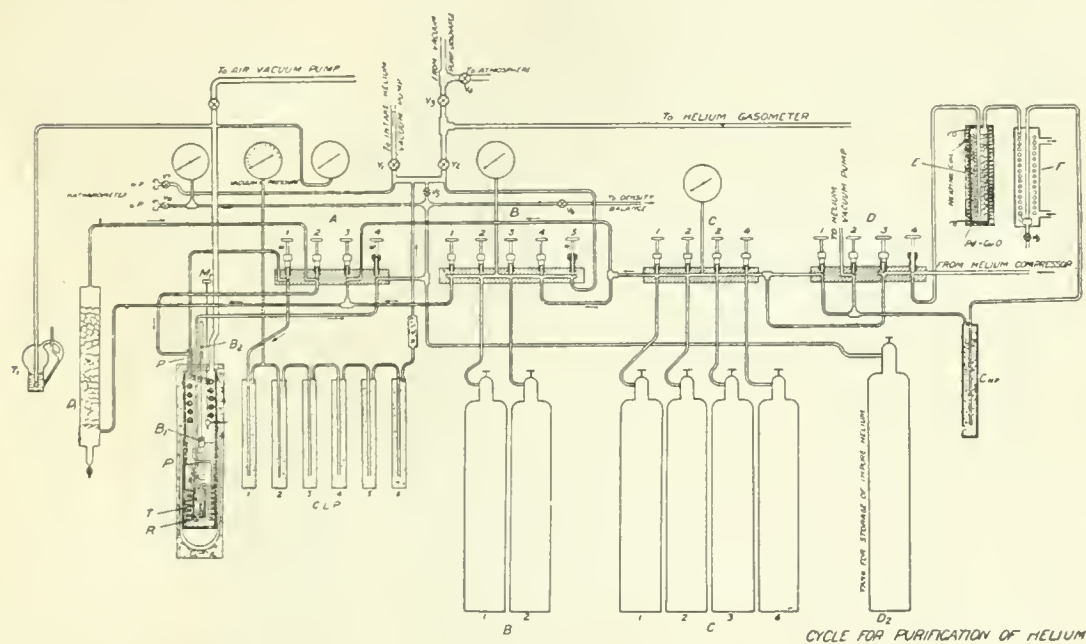


FIG. 5

cooled by means of liquid air, and then to the helium gasometer. The level of the liquid air was shown by the indicator *B*<sub>2</sub> attached to the cork float *B*<sub>1</sub>. The valve *M*<sub>1</sub> controlled the supply of liquid air that was drawn over into the apparatus from the store containers. In the construction of the apparatus, care was taken to reduce its size to a minimum, so that the consumption of liquid air would not be great, even though the process of purification was necessarily a discontinuous one. The impure helium given off by the charcoal, when heated, and that from the exhaustion of the conduits was carefully collected and the impurity separated out by condensation with liquid air as described above.



The Helium from the gasometer was compressed by the modified Whitehead compressor, described in Communication II, Section II. At high pressure the gas was passed through the bomb *E* filled with CuO and palladiumised asbestos and maintained at 400°C. Thus any traces of hydrogen that may have contaminated the gas in any way were made to combine with oxygen, the water produced being carried over and condensed in *F*. Finally the gas was passed at high pressure over the coconut charcoal tube *C.H.P.* and then delivered to the liquefier or stored in the cylinders. This cycle for purification proved to be an excellent one, since there was no evidence at any time of any blocking of the expansion valve or of the very small capillary tubes that make up the expansion coil in the liquefier.

(3) *The Helium Liquefier*.—In the design and construction of the helium liquefier, special attention was given to the problems of heat insulation and heat capacity. The principle of the apparatus has been explained in section (1). The helium was pre-cooled with liquid air and later liquid hydrogen boiling at a pressure of 6 cms. of mercury. At this temperature the Joule-Thomson effect was sufficient, in conjunction with the application of regenerative cooling, to condense the helium to a liquid. The apparatus is represented diagrammatically in Fig. 6 and Plate I “b” is a photograph of it as it was installed in the laboratory. The gas from the compressor entered as indicated in the figure. It passed successively through the coils  $D_1D_2$  and  $D_3D_4$  arranged in parallel. It then entered  $P_1$  and  $P_2$  also in parallel and afterwards passed successively through  $P_3P_4$  and  $P_5D_2D_4$ .  $P_1$  and  $P_3$  were cooled by the cold hydrogen vapour as it was drawn off by the hydrogen vacuum pump.  $D_1$ ,  $D_3$ ,  $P_2$  and  $P_3$  were cooled by the expanded helium from the expansion valve, as it passed to the gasometer.  $D_4$  served for the final pre-cooling, and was surrounded by liquid hydrogen boiling under a pressure of 6 cms. of mercury. The dimensions of these exchangers were chosen so that a very even and efficient interchange of temperature was assured. This was demonstrated by the fact that the outgoing expanded helium gas and also the evaporated hydrogen both remained very close to the room temperature throughout the operation. *T* was a trap whereby the gas was freed from the last traces of oil or water vapour.  $B_1$  and  $B_2$  were bombs containing charcoal. These were cooled with liquid air during the operation, and absorbed any gaseous contamination introduced during the operation of the cycle. The level of the liquid hydrogen in the refrigerator was determined by means of copper constantan thermocouples, or alternatively by helium thermometers with reservoirs at  $M$  and  $M_2$  and connected with a mercury mano-

meter by the steel tubes at  $G_2$ . The liquid hydrogen from the large metal containers was first transferred to the unsilvered flask  $F$ . This flask was protected by an outer silvered flask  $F_2$  containing liquid air.  $F_2$  had two unsilvered vertical observation strips on either side, so that the level of the liquid hydrogen in  $F_1$  could be seen directly. The valve  $C_1$  controlled the intake of the liquid hydrogen from  $F_1$  to the refrigerator. The valve  $C_2$ , with its corresponding spindle, controlled the expansion nozzle at the bottom of the coil  $P_5$ . The efficiency of the regeneration of the expansion-coil  $P_5$  was assured by

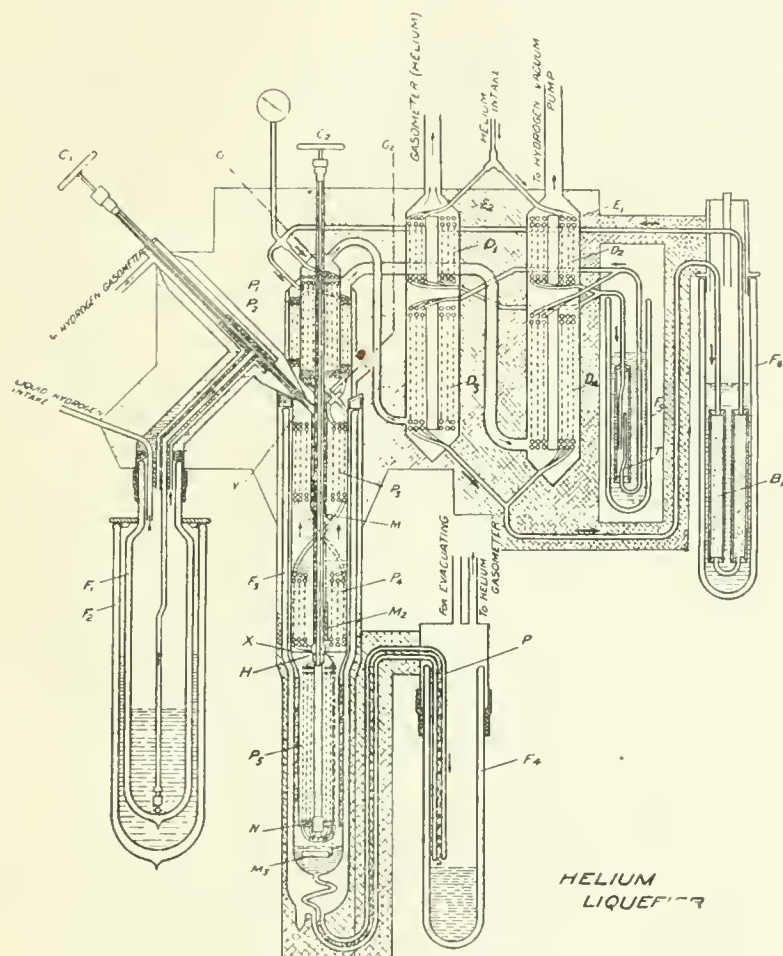


FIG. 6

fitting closely over it a very thin German silver envelope and soldering it at  $X$  to the bottom of the German silver container for liquid hydrogen. The expanded helium was thus forced to go through the interstices of the expansion coil in order to enter the holes at  $H$  in the tube surrounding the expansion valve spindle. The temperature of the region beneath the expansion valve was determined by a helium gas thermometer connected with a German silver reservoir at  $M_3$  and a steel capillary  $G_1$ . The protecting flask  $F_3$  was provided with a

specially designed siphon tube  $P$ . This tube was double-walled and protected by silvered walls and an intervening vacuum in the same manner as a Dewar flask. The flask  $F_4$  could be made either totally silvered or partially silvered with a plain portion at the bottom. In the latter case, it was protected by a plain vacuum flask containing liquid hydrogen and this, in turn, by a plain vacuum flask containing liquid air.

(d) *The Experiments*

Many unfortunate delays were experienced during the assembling and testing of the apparatus. Finally, on January 9th, 100 litres of liquid air were prepared. The following day thirty litres of liquid hydrogen were made and stored in 2 large copper containers, as described in (a). The various flasks for the Helium liquefier were then very carefully cooled with cold gaseous air and finally with liquid air. The apparatus and conduit pipes were all filled with pure helium. The helium was then circulated through the liquefier and at the same time the bombs  $B_1$  were kept immersed in liquid air. This was continued until the thermocouples in the hydrogen refrigerator indicated a temperature of  $-185^{\circ}\text{C}$ . The pressure of the helium was then raised to 100 atmospheres and the refrigerator surrounding the coil  $P_4$  filled with liquid hydrogen. The helium thermometer indicated for some time a gradually falling temperature at the expansion valve. Finally the mercury gauge attached to the helium thermometers indicated that a steady temperature  $-269^{\circ}\text{C}$ . was reached and after a few minutes, as the pressure at the expansion valve was lowered, the liquid helium could be seen collecting in the bottom of the flask. The operation was carried on until the supply of liquid hydrogen was exhausted and in all over a litre of liquid helium was obtained. Two weeks later a second successful liquefaction was demonstrated to a public audience. At this second time not more than 10 litres of liquid hydrogen were used to produce a litre of the liquid helium. The liquid helium remained steady for an hour during the demonstration.

The meniscus of the liquid helium was observed to be quite clear and distinct. The fluctuations due to expansion of the gas at the nozzle were clearly visible at the surface of the liquid. The liquid was colourless, much like liquid hydrogen, but the meniscus was entirely different from that of hydrogen. There was very little ebullition when the unsilvered flask was protected by means of liquid air only, and the surface remained quite smooth and undisturbed when



a protection of liquid hydrogen was provided. Samples of the gas evaporating from the liquid were collected and an analysis showed no traces of hydrogen. The purity of the helium was, however, beyond doubt as the liquid was perfectly clear and the expansion valve worked quite freely throughout the entire operation.

### *Summary*

The cryogenic laboratory at the University of Toronto is now equipped and has in operation all the essential apparatus for the liquefaction of air, hydrogen and helium. This equipment has been fully described in the three Communications upon the subject. By means of a suitable cryostat it will now be possible to produce and maintain for several hours any temperature in this region from  $0^{\circ}\text{C}$ . to  $-270^{\circ}\text{C}$ . When liquid helium is used in conjunction with the liquid cryostat temperatures between  $-269^{\circ}\text{C}$ . and  $-272^{\circ}\text{C}$ . may be maintained, and, in conjunction with the helium vapour cryostat, temperatures from  $-259^{\circ}\text{C}$ . to  $-269^{\circ}\text{C}$ . may be obtained. The importance of the work is emphasized when it is realized what a large field for low temperature research is opened up by the filling in of this temperature gap  $-259^{\circ}\text{C}$ .  $-272^{\circ}\text{C}$ .

In presenting this paper, the authors wish to acknowledge their indebtedness to Professor Kammerlingh Onnes of Leiden, Holland, the pioneer and outstanding authority upon research in this region. He not only very materially assisted through correspondence and conversation with Professor McLennan, but he also furnished him with drawings of the installations at Leiden.

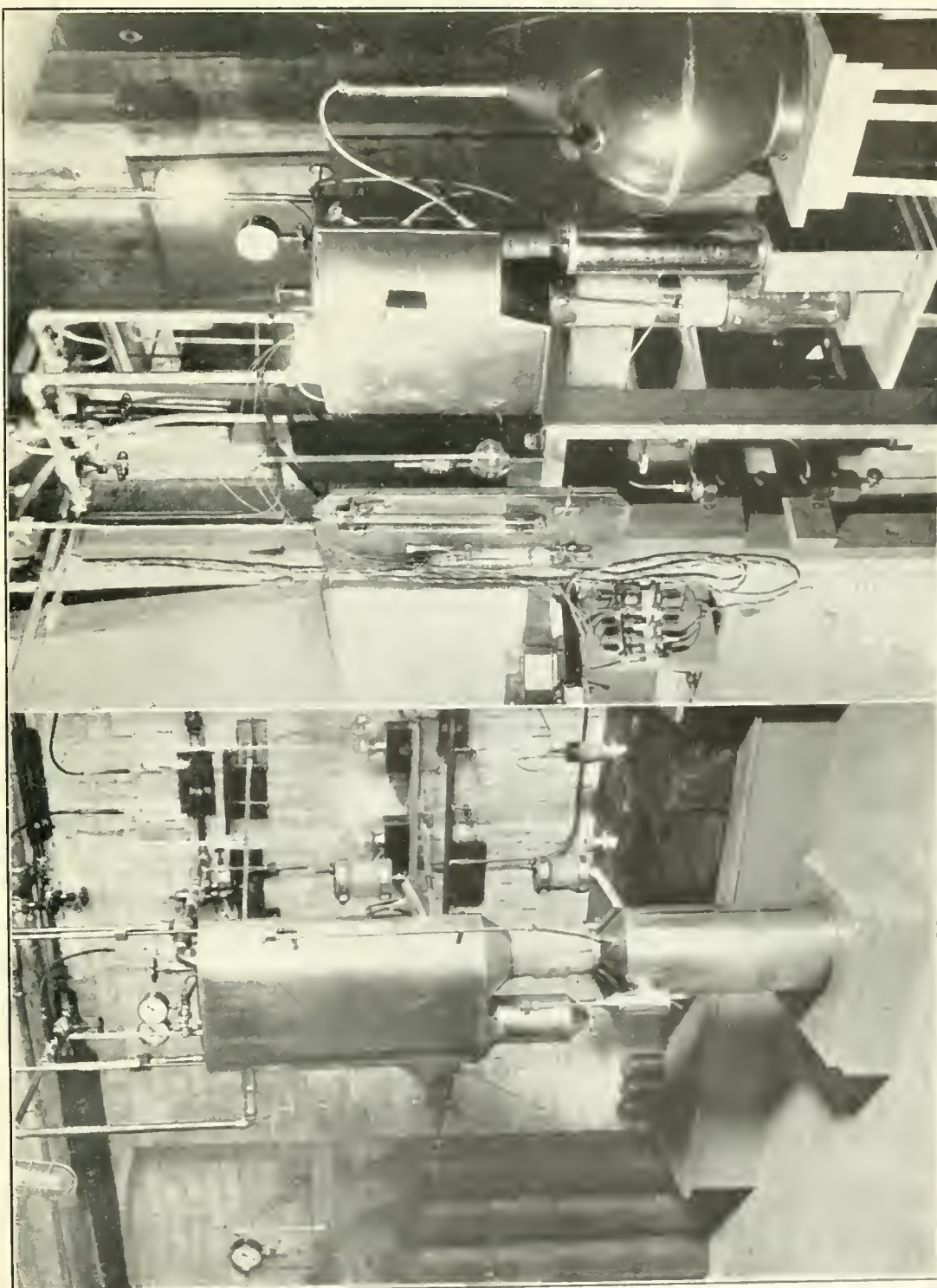
Mr. R. J. Lang, M.A., of the University of Alberta, also assisted by making very accurate analyses of the content of the helium gas during the process of purification.

This work was made possible through the financial assistance received from the Honorary Advisory Council for Scientific and Industrial Research of Ottawa, from the Carnegie Foundation for Research of New York, and from the University of Toronto.

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The Physical Laboratory,  
University of Toronto,  
February 15th, 1923.





"a"

"b"











Photomount  
Pamphlet  
Binder  
Gaylord Bros. Inc.  
Makers  
Syracuse, N. Y.  
PAT. JAN 21, 1908

Author Shrum, Gordon Merritt  
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